

CHEMICAL VAPOR DEPOSITION OF YTTRIA-STABILIZED ZIRCONIA AS A
THERMAL BARRIER COATING FOR GAS TURBINE ENGINES

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE
UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2004

ACKNOWLEDMENTS

First, I would like to thank Dr. Tim Anderson, who is my chief advisor and the Associate Dean for Research for the College of Engineering at the University of Florida. I appreciate his patience and his knowledge in the field of thermodynamics. I appreciate all his efforts to help me understand how important thermodynamics is to the field of chemical engineering.

I would also like to thank my committee, who have been very instrumental in my development as a professional. Dr. Crisalle showed me the essence of teamwork and hard work when I participated in the teaching assistant program at the University of Florida. Other characteristics that Dr. Crisalle showed me were organization, focus, and thoroughness. Most importantly, Dr. Crisalle will be a lifelong friend. Dr. Weaver has given me tremendous insight into surface chemistry. I also consider him a great friend and hope that he and I can collaborate in the future.

Special thanks are given to Shirley Kelly, Peggy-Jo Thran, Debbie Sandoval, Janice Harris, and Nancy Krell. These wonderful ladies are members of the support staff in the Chemical Engineering Department at the University of Florida. I would like to thank Dr. Gerhard Fuchs for his insight into the subject matter of this thesis. Finally, I would like to thank Dr. Theodore Besmann for the opportunity to work at Oak Ridge National Laboratory and for his guidance in achieving the goals of this work.

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Abstract of Dissertation Presented to the Graduate School of the University of Florida
in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

CHEMICAL VAPOR DEPOSITION OF YTTRIA-STABILIZED ZIRCONIA AS A
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August 2004

Chair: Tim Anderson

Major Department: Chemical Engineering

The gas turbine engine uses an yttria-stabilized zirconia (YSZ) coating to provide thermal insulation for its turbine blades. This YSZ coating must be tetragonal in crystal structure, columnar in microstructure, and be 100–250 μm thick to provide for adequate protection for the turbine blades in the severe engine environment. Currently, YSZ coatings are fabricated by electron-beam physical vapor deposition (EB-PVD), but this fabrication method is cost intensive. Chemical vapor deposition (CVD) is a more commercially viable processing method and a possible alternative to EB-PVD. The deposition of tetragonal YSZ from gaseous metal and oxidation sources were studied.

A chemical equilibrium analysis modeled the feasibility of depositing tetragonal YSZ for both chloride CVD ($\text{Zr-Y-C-O-Cl-H-Inert}$ system) and metal-organic CVD (MOCVD) (Zr-Y-C-O-H system). Pure thermochemical properties and the assessed YSZ phase diagram were used in this analysis. Using the molar input of metals ($(n_Y + n_{\text{Zr}})$ and $(n_Y / (n_Y + n_{\text{Zr}}) = 0.08)$) as bases, equilibrium calculations showed that tetragonal YSZ

formation was feasible. Tetragonal YSZ formation was feasible with high oxygen content ($n_O / (n_Y + n_{Zr}) > 8$) and high temperature ($T > 100^\circ\text{C}$) in the case of chloride CVD (Zr-Y-C-O-Cl-H-Inert). Tetragonal YSZ formation was feasible with high oxygen content ($n_O / (n_Y + n_{Zr}) > 5$) and high temperature ($T > 950^\circ\text{C}$) in the case of MOCVD (Zr-Y-C-O-H). Although solid carbon formation did not appear in chloride CVD, additional oxygen ($n_O / (n_Y + n_{Zr}) > 32$) and low hydrogen content relative to carbon ($n_H / n_C < 2$) were required to avoid solid carbon formation in MOCVD.

Coatings were deposited using a set of base conditions derived from the chemical equilibrium analysis. In chloride CVD, YCl_3 was not included because of its low vapor pressure, thus, ZrCl_4 was oxidized with the $\text{H}_2\text{-CO}_2$ gas mixture. Monoclinic ZrO_2 coatings were deposited at the thermochemically optimized conditions ($n_O / (n_Y + n_{Zr}) > 8$, $T > 1004^\circ\text{C}$) with approximately $5.5 \mu\text{m h}^{-1}$ growth rate.

In metal-organic CVD (MOCVD), liquid precursor solutions of Y- and Zr- β -diketonate and Y- and Zr-*n*-butoxide precursors were used as the metal sources and O_2 gas was used as the oxidation source. Using the Y- and Zr- β -diketonate liquid precursor solution, tetragonal YSZ was deposited with a layered microstructure apparent and a maximum growth rate of approximately $14 \mu\text{m h}^{-1}$ (activation energy (E_a) of $50.9 \pm 4.3 \text{ kJ mol}^{-1}$). The growth rate (approximately $43 \mu\text{m h}^{-1}$ with $E_a = 53.8 \pm 7.9 \text{ kJ mol}^{-1}$) was improved using Y- and Zr-*n*-butoxide liquid precursor solutions, and the microstructure was columnar. Yet, two-phase deposition of monoclinic ZrO_2 and tetragonal YSZ occurred. Results of electron-probe micro-analysis showed that the $n_Y / (n_Y + n_{Zr})$ ratio was less than 45% of the $n_Y / (n_Y + n_{Zr})$ ratio in the liquid precursor solution.

CHAPTER 1 INTRODUCTION

Demand for lower cost power generation has spurred research efforts toward lower-cost materials fabrication. A key power generating device known as the gas turbine, has garnered much attention because of its efficient power generating capabilities. Yet, the gas turbine incurs high capital and maintenance costs because of its complex materials design and function. Thus, improvements in materials and fabrication will boost the gas turbine's overall lifetime and efficiency and potentially reduce capital and maintenance costs.

Cost efficiency, engine efficiency and engine lifetime are partially limited by turbine blade performance and cycle life (Haynes 1997, Miller 1997). The turbine blades (which are the moving part of the turbine) require protection from exposure to hot combustible gases associated with the engine environment. A thermal barrier coating is used to protect these turbine blades from high temperatures and contaminants in the fuel and intake air (Haynes 1997, Marple 2000).

This study focuses on the cost-efficient fabrication of thermal barrier coatings. The ceramic, yttria-stabilized zirconia (YSZ) is used since it has adequate high-temperature properties necessary for gas turbine environments (Wahl *et al.* 2001a). Currently, YSZ is fabricated using air plasma spray (APS) or electron-beam physical vapor deposition (EB-PVD), however, these techniques are capital- and operational-cost intensive (Wahl *et al.* 2001b). An economical alternative, chemical vapor deposition

(CVD) shows promise as a possible replacement for APS or EB-PVD (Krumdieck *et al.* 2003, Wahl *et al.* 2001a, Wahl *et al.* 2001b, Pulver and Wahl 1997).

The goal of this work is the successful deposition of YSZ using the CVD method. This work uses a chemical equilibrium analysis to identify, optimize, and determine the effect of CVD conditions on gas and solid phase formation. The CVD conditions used were atom mole ratios (e.g., the ratio of the total number of hydrogen atoms in the system to the total number of carbon atoms in the system, regardless of which molecules they reside in), the substrate temperature, and the reactor pressure. These optimized CVD conditions were used as a basis for selecting experimental conditions. Further, the equilibrium analysis was used to explain experimental results.

Experiments were attempted in a CVD reactor. A vertical, cold-wall, stagnation flow reactor was implemented in this work. Among the myriad of possible precursors, only three types were used. For chloride CVD, HCl reacted with Zr chips to provide a controllable Zr vapor source. For MOCVD, Y- and Zr- β -diketonates and Y- and Zr-*n*-butoxides were used. Since the experiments used liquid delivery, a tetrahydrofuran (THF) solvent was used to dissolve the Y- and Zr- β -diketonates and toluene and *n*-butanol were used to dissolve Y- and Zr-*n*-butoxides, respectively.

To analyze the coating deposition, several characterization tools were used. For crystal structure analysis, x-ray diffraction (XRD) was used. For coating morphological analysis, scanning electron microscopy (SEM) was used. For coating compositional analysis, electron probe micro-analysis (EPMA) was used.

The next chapter follows with a background into why yttria-stabilized zirconia is used as a thermal barrier coating and why CVD can be used to fabricate this material.

The following chapter delves into the chemical equilibrium analysis to optimize the atom ratios and intensive variables (temperature and pressure). Then, the following chapter describes the experimental approach for CVD and materials characterization. The following three chapters present and discuss the results of experimental efforts. The last chapter then summarizes, concludes, and recommends possible avenues for future work.

CHAPTER 2 BACKGROUND

2.1 Introduction

The major components of a gas turbine engine include a compressor, a combustor and a turbine (Owen *et al.* 1991). A schematic of an aircraft engine is shown in Figure 2-1. In this engine, the intake air fan (1) draws air in at approximately 10°C, 0.9 atm, and 525 km h⁻¹ (normal commercial aircraft cruising speed). This air is compressed (2) to approximately a 20:1 (or higher) ratio. The pressurized air is directed into the combustor (3), where high temperature combustion occurs with jet fuel, which is sprayed by spray nozzles. The combustion reaction, which is necessary to provide engine thrust, usually takes place between 1000°C and 1200°C. The exhaust from the combustor is expanded through a turbine (4), which provides mechanical work and electrical power for the engine. Air cooling ducts (5) are used to carry heat away and prevent melting of the hot engine components (Owen *et al.* 1991). Finally, the air is exhausted through the thrust nozzle (6) at a speed four times that of the intake air.

The turbine's performance is limited by blade fatigue, which is caused by the severe operational conditions. A set of blades, situated on a rotor-stator assembly, are found within the turbine. These blades are rapidly rotated and undergo severe thermo-mechanical stresses (Haynes 1997). This stress cause the eventual fatigue of the blade (after approximately 8000 h of service) and necessitates frequent maintenance schedules of the engine (Kimmel *et al.* 2000)

Blade fatigue is slowed, however, with Ni-based super-alloys, which are used as the cast blade material (Henderson *et al.* 2002). The Ni-based super-alloy is preferred because of its adequate high-temperature creep resistance (Henderson *et al.* 2002). This high-temperature creep resistance means that the plastic deformation and eventual degradation associated with high temperature thermal cycling is slowed. Typical super-alloys are Mar-M247 (Caterpillar, Peoria, IL) or Rene-N5 (General Electric Aircraft Engines, Cincinnati, OH).

It was observed, however, that blade lifetime can be extended and, thus, extend engine lifetime by overlaying protective coatings (Stiger *et al.* 1999). A favorable consequence of increased engine lifetime is reduced operational costs for gas turbine operators. The entire protective coating system is known as a thermal barrier coating (TBC) system.

2.2 Thermal Barrier Coating (TBC) System

The state-of-the-art TBC system is shown in Figure 2-2. The TBC consists of a turbine blade alloy material, an oxidation-resistant bond coat, an oxide-scale interface, and a thermally insulating, ceramic top coat (He *et al.* 2000, Clarke and Levi 2003). Overlaying the blade is a Ni-Al bond coat (~50-75 μm thick), which acts as an additional oxidation barrier. The Ni-Al coatings are preferred since an oxidation resistant alumina (Al_2O_3) scale forms during high temperature thermal cycling (Miller 1997). This alumina-scale has low oxygen diffusivity through its thickness (Brady *et al.* 2000, Birks *et al.* 1994).

The bond coat (after pre-oxidation to form the alumina-scale) has an overlaying EB-PVD YSZ top coat (~100-250 μm thick), which acts as a thermal barrier. The 6-8

wt.% YSZ has a low thermal conductivity ($0.02\text{--}0.025\text{ W cm}^{-1}\text{ K}^{-1}$) at normal turbine operating temperatures (Nicholls 2003, An *et al.* 1999). Further, YSZ functions as a corrosion-resistant barrier by minimizing the ingress of contaminants (such as salts in the intake air of the engine or sulfur in the jet fuel) to the underlying metal-alloy (Haynes 1997).

The TBC system offers several key benefits to the gas turbine engine. First, the TBC reduces the blade temperature by as much as 200°C (Wahl *et al.* 2001a). This increases the thermal efficiency of the turbine since the TBC reduces blade air-cooling and increases the allowable turbine inlet air temperatures (Brady *et al.* 2000b, Owen *et al.* 1991). This increase in turbine inlet temperature allows for a higher fuel-burning temperature, which translates to higher fuel efficiency and subsequent fuel cost savings. All of these advantages illustrate the overall benefit of using TBCs.

2.3 Evolution of the TBC System

The first TBCs originated in the 1950s when nichrome was used to protect thruster components in the X-15 experimental rocket plane (Miller 1997). These Ni-based coatings eventually served as the blade material in aircraft engines (Miller 1997, Stiger *et al.* 1999). Since then, the blade alloy incorporated aluminum because of the formation of an alumina ($\alpha\text{-Al}_2\text{O}_3$)-scale during engine thermal cycling. Alumina scales demonstrated low or no volatility, good phase stability, and strong adherence to the underlying blade during turbine operation (Brady *et al.* 2000a, Mevrel 1989, Stott *et al.* 1999).

The bond coat, which was also originally nichrome, was introduced during the late 1950s and early 1960s as an additional oxidation barrier for the turbine blade (Miller

1997). In high temperature engine operation, a chromia scale layer formed. This chromia scale, however, formed highly volatile suboxides during engine operation (Brady *et al.* 2000). These suboxides were considered undesirable since they re-condensed and damaged engine parts (Brady *et al.* 2000). To improve its engine durability, the bond coat was cast into a Ni-Al alloy during the late 1960s (Miller 1997).

Although longer-lasting than nichrome, these Ni-Al alloys exhibited short lifetimes because of the rapidly growing alumina scale. In the 1970s, reactive-elements (such as Y and Cr) were added to the Ni-Al system. The addition of chromium (~1-3%) and yttrium (~0.3%) slowed the diffusion of aluminum through the bond coat (Haynes 1997). The slow-diffusing aluminum slowed alumina scale growth and aluminum depletion during thermal cycling. The slow diffusion of aluminum, thus, added lifetime to the bond coat (Haynes 1997, Miller 1997). Recently, platinum addition to the bond coat and sulfur removal from the bond coat (no Cr or Y addition) increased scale adherence and further increased the protective lifetime of the bond coat (Stott *et al.* 1999, Lee *et al.* 1998, Zhang *et al.* 2001).

Despite its benefits, the alumina scale was not thick (~2-5 μm) enough to provide any turbine efficiency gains (Miller 1997, Brady *et al.* 2000). Zirconia-based ceramics were added during the 1970s to address increasing the turbine thermal efficiency by overlaying a thermally insulating layer (Miller *et al.* 1997, Stiger *et al.* 1999).

2.4 Zirconia-Based Ceramics

Pure zirconia has excellent thermal insulating properties because of its low thermal conductivity, however, it has issues with regard to its phase stability. These issues stem from the phase transformation in zirconia. Before delving into that

discussion, a review is given regarding the atomic arrangement of the crystal lattice for each zirconia phase.

Pure zirconia is stable in the monoclinic phase (Mss) up to 970°C (Figure 2-3) (Stubican *et al.* 1982, Stubican 1988, Scott *et al.* 1975, Pascual and Duran 1983, Suzuki 1995). The monoclinic crystal structure (Figure 2-4) shows both trigonal and tetrahedral symmetry (between the Zr and O atoms). Above 970°C, monoclinic zirconia undergoes phase transformation to the tetragonal crystal structure (Tss, Figure 2-3). In this crystal lattice, a full octet of oxygen atoms resides in the unit cell, with two sets of tetrahedral coordination (Figure 2-5).

Pure zirconia coatings, however, were not suitable for the turbine thermal cycling temperature range (25–1200°C) because they endured a dramatic volume reduction upon phase transformation. During phase transformation, pure zirconia undergoes a 9% decrease in volume (theoretical density change from 5.560 g cm⁻³ for monoclinic zirconia to 6.100 g cm⁻³ for tetragonal zirconia) because of the anisotropic contraction of the crystal lattice (all lattice parameters decrease at differing amounts) (Kelly and Rose 2002, Subbarao 1981). This phase transformation is diffusion-less (martensitic) since the atoms rearrange their lattice positions without displacing any more than one atomic diameter away from their original position and retain their nearest neighbors (Subbarao 1981, Kelly and Rose 2002). The end result of continued thermal cycling (and continued tetragonal-to-monoclinic phase transformation) is crumbling of the bulk ceramic, large-scale buckling at the top coat-scale-bond coat interface, and catastrophic delamination of the zirconia coating from the blade (Subbarao 1981, Wright and Evans 1999, Schulz 2000).

Di- or tri-valent dopant oxides (i.e., calcia or yttria), which have cubic symmetry, were used to minimize dramatic phase transformation by “partially-stabilizing” zirconia (Miller 1997, Subbarao 1981). The intent was to lessen the effect of (or to avoid) the tetragonal-monoclinic phase transformation by doping enough of these di- or tri-valent oxides to cause the cubic phase of zirconia to be stable (Miller 1997). The first attempts of such doping were with calcia (to make cubic calcia-stabilized zirconia (CaSZ)). This ceramic was short-lived during thermal cycling because it lacked phase stability. The cubic phase of CaSZ is stable above 1140°C. Upon use, CaSZ undergoes severe volume changes because of such phase transformation and severe cracking occurs within the top coat. Thus, this ceramic endured approximately the same lifetime as pure monoclinic zirconia (Miller 1997).

Yttria doping in zirconia demonstrated great success as a fuel cell electrolyte (Minh 1995, Subbarao 1981). The act of doping yttria into zirconia replaced some of the Zr^{+4} cations with Y^{+3} cations. Yttria, when doped at 12-16 wt. % in zirconia, “fully stabilized” zirconia to be cubic in symmetry with the stable “CaF₂” structure (Minh 1995, Subbarao 1981). This structure has eight oxygen atoms that are tetrahedrally coordinated and equidistantly surrounding each zirconium atom with four zirconium atoms equidistantly surrounding each set of eight oxygen atoms (Subbarao 1981, Minh 1995).

In the case of TBC applications, yttria was added at approximately 6-8 wt. % to zirconia to partially-stabilize its crystal structure to the tetragonal phase. (Subbarao 1981, Miller 1997) This partial stabilization lowered the transformation temperature of zirconia to as low as 600°C (Figure 2-3). This lowering of the transformation temperature (coupled with the yttria doping) minimized the mobility of the lattice atoms (Kelly and

Rose 2002). This minimized atom mobility circumvented phase transformation, thus making the tetragonal phase meta-stable at room temperature (Miller 1997, Subbarao 1981).

Other advantages with tetragonal YSZ were better thermal shock resistance and better phonon scattering as compared to cubic YSZ. The better thermal shock resistance was due to the lower linear thermal expansion coefficient (Soyez *et al.* 2000). The increased phonon scattering was due to the lower thermal conductivity of tetragonal YSZ from the increased oxygen vacancies within the oxygen sublattice of the tetragonal phase (Soyez *et al.* 2000). Thus, tetragonal YSZ was preferred over cubic YSZ as a TBC.

2.5 Current Issues with TBCs

To this point, the discussion described the benefits of using tetragonal YSZ as a thermally insulating coating. There are two main issues facing current TBC technology: TBC fabrication and TBC lifetime. An understanding of these two issues gives insight into the nature of improving the TBC materials system.

2.5.1 Thermal Barrier Coating Fabrication

The two methods of fabricating the top coat are plasma spraying and electron-beam physical vapor deposition (EB-PVD). Plasma spraying was introduced in the early 1970's since it offered the flexibility to deposit both bond coats and YSZ top coats (Miller 1997). Plasma spraying uses finely divided yttria and zirconia surfacing materials deposited in a molten or semi-molten state onto a substrate to form YSZ (Kucuk *et al.* 2000a, Kucuk *et al.* 2000b). The drawback with plasma sprayed YSZ was the lamellar microstructure, which was strain-intolerant to thermal cycling (Haynes 1997).

A more strain-tolerant coating was developed using EB-PVD. EB-PVD (Pratt & Whitney, MA) was commercialized in the mid 1970's to fabricate YSZ (Miller 1997). This technique uses an electron-beam to vaporize molten yttria and zirconia mixtures in a high vacuum chamber and uses oxygen to deposit YSZ onto a hot blade at a high growth rate ($\sim 4\text{--}10\ \mu\text{m min}^{-1}$) (Schulz and Schmuker 2000). The coating has a columnar microstructure, which is more accommodating to thermal cycling (Miller 1997). This strain-tolerance to thermal cycling made EB-PVD coatings more useful than plasma sprayed YSZ coatings, thus, giving EB-PVD YSZ coatings a comparably longer lifetime.

EB-PVD is “line-of-sight” which leaves hidden areas uncovered, and results in significant spacing between columnar grains (Wahl *et al.* 2001a, Wahl *et al.* 2001b). Such spacing exposes parts of the bare metal to the high temperature combustible gases and contaminants in the engine environment. Further, it is not feasible to coat complex and internal geometries (for air-cooling the turbine blade) by EB-PVD (Wahl *et al.* 2001a). Finally, YSZ delamination often involves alumina scale delamination, which is detrimental (and expensive) since the complete bond coat had to be replaced along with the YSZ top coat (Haynes 1997).

2.5.2 Thermal Barrier Coating Lifetime

It has been shown that the TBC fabrication method strongly influences the mechanisms of delamination and TBC lifetime by the use of plasma spraying and EB-PVD. This section describes the general mode of TBC failure.

Failure testing of the TBC system involves the use of a rigorous thermal cycling test method adopted by the NASA Glenn Research Center (Cleveland, OH) (Vaidyanathan *et al.* 2000). This testing method studies the impact of an extreme engine

environment on the TBC material system in an effort to “over-engineer” these protective layers for longevity during commercial use. The testing rig is a hot wall furnace with testing zone that heats to as high as 1200°C (Vaidyanathan *et al.* 2000, Pint *et al.* 2001, Haynes *et al.* 2001). TBC specimens are inserted onto a metal rod that draws in the specimen through the furnace bottom (Pint *et al.* 2001). The specimen endures continuous 1-h thermal cycling that consists of 10 minutes of air-cooling after 50 minutes of hot-zone exposure in flowing oxygen (HPLC grade) (Vaidyanathan *et al.* 2000, Pint *et al.* 1998). The coating undergoes continuous thermal cycling until failure occurs. Failure of the specimen was defined as 50 to 100% delamination of either the alumina scale or the YSZ top coat (Figure 2-6 and Figure 2-7). This failure is due to the growth and subsequent delamination of the alumina scale or ceramic top coat and is signified by significant weight loss of the sample as a function of increasing 1-h thermal cycles (Haynes *et al.* 2001).

Despite its benefits, the tetragonal YSZ top coat inevitably delaminates. Typically, APS YSZ delaminates after approximately 400 1-h thermal cycles (Miller 1997) and EB-PVD YSZ delaminates after approximately 1200 1-h thermal cycles (Vaidyanathan *et al.* 2000). In both types of fabricated coatings, ceramic delamination is due to thermal stresses imposed on the TBC system during thermal cycling. Thermal stresses are owed to the coefficient of thermal expansion (CTE) mismatch between the metal and ceramic layers (Sergo and Clarke 1998). As the blade-bond coat-top coat system is thermally cycled, the CTE mismatch ($\Delta\text{CTE} = 5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$) between the YSZ top coat and the metal bond coat imparts tensile stress in the top coat (Hass *et al.* 2001). To compound this top coat-bond coat CTE mismatch during thermal cycling, an alumina-

scale layer forms between the bond coat and top coat. The CTE mismatch ($\Delta\text{CTE} = 4.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$) between the alumina scale and the YSZ imparts compressive stresses on the YSZ-alumina scale-bond coat interface during thermal cycling (Hass *et al.* 2001). These stresses are in-plane to the ceramic-metallic interface, causing residual strain and eventual delamination at the alumina scale-top coat interface or at the alumina scale-bond coat interface (Padture *et al.* 2002).

The mode of failure was briefly described above and is beyond the scope of this work. The reviews by Wright and Evans 1999, Padture *et al.* 2002, Evans *et al.* 2001, and Levi 2002, Miller 1997 and papers by Soyeyz *et al.* 2000 and Vaidyanathan *et al.* 2000 give insight into the mechanisms of thermo-mechanical failure. Another type of failure, due to chemical effects from the bond coat, are detailed by Smialek 2001, Pint *et al.* 1998, Pint *et al.* 2002, Lee *et al.* 1998, Zhang *et al.* 2001, Smialek 2001, Haynes 2001, Pint *et al.* 2001, and Haynes *et al.* 1999.

2.6 Chemical Vapor Deposition (CVD): A Viable Alternative

If a viable alternative fabrication method is developed, it must meet the following requirements. First, the processing method must efficiently fabricate strain-tolerant, columnar-grained YSZ top coats. Second, the top coats must demonstrate comparable or better accommodation for thermal cycling (Wahl *et al.* 2001 a). Finally, this processing method must be cost-effective and less expensive than EB-PVD.

CVD is a viable alternative to EB-PVD since it is cost-effective and has shown success as an alternative method for bond coat fabrication (Pint *et al.* 2002, Zhang *et al.* 2001, Haynes *et al.* 2002). CVD of oxide coatings involves the reaction of metal source

gases with an oxygen source to grow metal oxide films. The metal oxide of interest, YSZ, is discussed below as it pertains to high growth rate coating for TBC applications.

2.7 Chemical Vapor Deposition of Yttria-Stabilized Zirconia (YSZ)

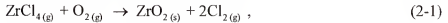
Given the success of the (Ni, Pt)-Al as a bond coat material, it is reasonable to apply the CVD method to the top coat. Chloride CVD is the method of choice for bond coats, and it is also useful to investigate metal-organic CVD (MOCVD) given its wide success of fabricating YSZ fuel cell electrolytes (Wang *et al.* 2000, Krumdieck *et al.* 2003, Song *et al.* 2003, Akiyama *et al.* 1995) and high temperature buffer layers for $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ superconductors (Jun *et al.* 2003, Kim *et al.* 1995, Kubota *et al.* 2001).

In general, CVD has several advantages over the APS, and EB-PVD coating methods. First, metal-chloride precursor vapor pressures (Yamane and Harai 1989, Shiau 1989, Pashinkin *et al.* 1950) and metal-organic precursor vapor pressures (Matsuno *et al.* 1992, Fulem *et al.* 2004, Colominas *et al.* 2001) are relatively high as compared to the refractory ceramic sources (liquefied to temperatures in excess of 2700°C), which are used in EB-PVD and plasma spray (Stubican 1988, Suzuki 1995). The high vapor pressures make precursors transport easier to a blade surface as compared to plasma sprayed or EB-PVD powder precursors. Second, CVD has shown that columnar microstructures can be obtained (Krumdieck *et al.* 2002). Third, CVD offers large area coverage, making large geometries easier to coat without the use of complex robotics (Wahl *et al.* 2001a). Finally, CVD offers great doping control, making hetero-metallic oxide layers, such as YSZ, easier to deposit (Jones and Chalker 2003).

2.7.1 Chloride CVD of YSZ

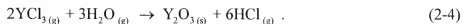
In chloride CVD, the metal chlorides, YCl_3 and ZrCl_4 , react with an oxygen source, such as O_2 (Wahl *et al.* 1979, Yamane and Harai 1989), H_2O (Cao *et al.* 1993), or a gas mixture of CO_2 and H_2 (Brennfleck *et al.* 1981; Minet *et al.* 1986, 1987; Sipp *et al.* 1992a, 1992b) to deposit YSZ onto a substrate. For efficient deposition of tetragonal YSZ TBCs, the growth rate must be on the order of 40 to $50 \mu\text{m h}^{-1}$ (Tu *et al.* 2002, Wahl *et al.* 2001a) This means that to maximize growth rates, the choice of an oxygen source is critical because this maximized surface oxygen for surface metal oxide formation (Minet *et al.* 1987).

There are three common oxidizing methods for depositing YSZ with chloride CVD. One method is by direct reaction with O_2 (Yamane and Harai 1989).



With this technique, Yamane and Harai demonstrated that the yttria composition in the cubic YSZ films was controlled by a linear dependence on the inlet $\text{YCl}_3/(\text{YCl}_3 + \text{ZrCl}_4)$ molar ratio. This linear dependence suggested that the yttrium content in tetragonal YSZ can also be controlled. These workers obtained low growth rates ($\sim 1.5\text{--}2.0 \mu\text{m h}^{-1}$), which were inadequate for commercial TBC fabrication. Although there was no specific reason given for the low growth rate, the low overall flow rate ($\sim 170 \text{ ml min}^{-1}$) and high yield of homogeneously nucleated YSZ powders in the gas phase may have contributed to insufficient transport of the reactants to the substrate and the subsequent low growth rate (Yamane and Harai 1989).

Another method to oxidize the metal chloride precursors is using water vapor (Cao *et al.* 1993).

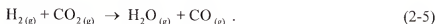


Cao *et al.* (1993) obtained cubic and tetragonal YSZ films for pore filling within α -alumina substrates, but their growth rates were as high as $0.08 \mu\text{m h}^{-1}$. Although there was no specific reason given for the low growth rate, the low transport ($\sim 7 \text{ ml min}^{-1}$) of reactants to the substrate surface and significant homogeneously nucleated YSZ powders may have contributed to the low growth rates (Cao *et al.* 1993). Further, Cao *et al.* (1993) used a forced jet of water into a flowing gas stream of argon at 100°C . This type of oxygen source delivery method was inadequate since the amount of water carried into the reactor may vary depending on water jet velocity, time of water molecules at temperature, carrier gas velocity, etc. Since no information was given in this work with regard to the optimization of these variables on the actual molar delivery rate of water vapor, this technique was considered unreliable.

Although the methods just mentioned show the feasibility of obtaining cubic YSZ, the growth rates were inadequate for TBC fabrication. Minet *et al.* (1986) explained that direct reaction of ZrCl_4 and YCl_3 with O_2 or H_2O created such an irreversible reaction that homogeneous nucleation occurred. Homogeneous nucleation creates unwanted pre-reacted powders of metal oxides that can minimize the growth rate and diminish coating quality.

To solve the problem of powder formation, Wahl *et al.* (1979) used the reverse water gas shift reaction (RWGSR) to control the amount of water vapor formed during

deposition. The RWGSR controls water vapor formation by the H_2 reduction of CO_2 (Tingey 1966),



The rate of this reaction is very slow in the forward direction below $800^\circ C$ (Tingey 1966). As the temperature exceeds $800^\circ C$, significant H_2O partial pressures are generated near the substrate surface, and rapid reaction with the metal chloride precursors ensue (Sipp *et al.* 1992a).

Because the RWGSR controls surface water molecule formation, it is an advantageous processing method for fabrication of many high temperature ceramics using cold-wall reactors (Sipp 1992a, Sipp *et al.* 1992b; Minet *et al.* 1987; Haynes *et al.* 1999). The most promising attempt by Sipp *et al.* resulted in high yttria growth rates ($\sim 17 \mu m h^{-1}$) using the RWGSR to oxidize YCl_3 (1992b). This success was attributed to a substrate temperature of higher than $1100^\circ C$, which leads to significant surface water formation. Currently, there is no evidence of previous attempts to deposit YSZ using the RWGSR. Available information is summarized in Table 2-1 for yttria, zirconia, and YSZ chloride CVD using the three oxidizing techniques. These favorable results of yttria and zirconia CVD using the RWGSR as an oxidation source shows promise that this technique will work for YSZ fabrication.

2.7.2 Parameters Influencing Chloride CVD Growth Rates

Chloride CVD parameters that influenced yttria and zirconia growth rates (by the RWGSR) were the substrate surface temperature, the YCl_3 , $ZrCl_4$, H_2 , and CO_2 reactant gas concentration, the overall pressure, and the overall gas flow rate (Sipp *et al.* 1992a). These CVD parameters must be optimized in the desired rate-limited regime: either mass-

transfer limited or surface-reaction limited (Park 2001). To maximize the growth rate, the mass-transfer limited regime is ideal since growth is steady-state and not kinetically limited due to the use of high temperature (Pierson 1992). A discussion of both regimes and how they influence the growth rate follows below.

On one hand, the growth rate is limited by surface temperature in the surface-reaction limited regime (Pierson 1992). This regime exists over a temperature range for which the deposition rate has an exponential dependence (Pierson 1992). Thus, the natural logarithm of the growth rate within this regime was assumed linearly dependent on the inverse substrate temperature (Arrhenius dependence). This Arrhenius dependence of the growth rate on temperature is given by,

$$r_{dep} = k_o \exp\left(-\frac{E_a}{RT}\right), \quad (2-6)$$

where r_{dep} is the growth rate ($\mu\text{m h}^{-1}$), k_o is the pre-exponential factor ($\mu\text{m h}^{-1}$), E_a is the activation energy (kJ mol^{-1}), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the absolute surface temperature (K) (Pulver and Wahl 2000). In most experimental work, E_a is estimated based on the growth rate data (Pierson 1992). This estimate is obtained by calculating the change in the natural logarithm of the deposition rate over the change in the inverse absolute growth temperature (Figure 2-8) (Pierson 1992). The term k_o is determined from the intercept of the line as it approaches $1/T = 0$ Figure 2-8.

On the other hand, the growth rate is limited less by surface temperature and more by reagent transport to the substrate surface from the bulk gas stream in the mass-transfer limited regime (Park 2001). In the mass-transfer limited regime, the growth rate (r_{dep} , $\mu\text{m h}^{-1}$) is dependent on the flux (J_A , $\text{g cm}^{-2} \text{ h}^{-1}$) of the precursor (A) to the substrate through the boundary layer (Holstein 1992),

$$r_{dep} \propto J_A. \quad (2-7)$$

The flux of the precursor through the boundary layer is directly related to the binary gas-phase diffusivity (D_{AB} , in $\text{cm}^2 \text{h}^{-1}$, where A is the precursors and B is the carrier gas), the precursor gas-phase mole fraction (y_A), and the gas density (ρ , g cm^{-3}) and inversely proportional to the viscous boundary layer thickness (δ , in $\text{cm}^{1/2}$) (Holstein 1992),

$$J \propto \frac{D_{AB} \rho y_A}{\delta}. \quad (2-8)$$

Equation (2-8) physically represents the ratio of the mass transfer of precursors ($D_{AB} \rho y_A$) to the mass transfer resistance owed to viscous dissipation of the gas flow near an impermeable surface (δ) (Holstein 1992, Bird *et al.* 1960).

The binary gas-phase diffusivity (D_{AB}) is proportional to the 1.5 power of temperature (in K), inversely proportional to the square root of the molecular weight of both the precursor (M_A , in g mol^{-1}), and carrier gas (M_B , in g mol^{-1}) and inversely proportional to the pressure (P , in Pa) (Bird *et al.* 1960),

$$D_{AB} \propto \frac{T^{3/2}}{P} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}. \quad (2-9)$$

The precursor gas-phase mole fraction (y_A) is related to the type of precursor introduction method used. For example, *an in situ* chlorination method reacts HCl or Cl_2 with a metal sponge or chips, which means y_A depends of the inlet moles of the reagents prior to chlorination divided by the total mole of gases added to the system. Another example includes the use of an *in situ* aerosol-assisted liquid delivery (AALD) method for which y_A depends on the molar precursor delivery rate and the precursor solubility in a carrier

solvent (Lane et al. 1998). In addition, the viscous boundary layer thickness (δ) is defined by (Holstein 1992),

$$\delta \propto \left[\frac{\mu}{\rho(a + \omega_{SPIN})} \right]^{1/2} \quad (2-10)$$

In Eq. (2-10), μ is the gas viscosity (in $\text{g cm}^{-1} \text{h}^{-1}$), a is the forced flow parameter (in h^{-1}) that is proportional to the gas velocity (in cm h^{-1}), and ω_{SPIN} is the substrate rotation rate (in rotations per hour). In this work, the substrate will not be rotated. Substitution of Eq. (2-9), Eq. (2-9), and Eq. (2-10) into Eq. (2-8) gives,

$$r_{dep} \propto \frac{\rho y_A T^{3/2}}{P} \left[a \left(\frac{1}{M_A} + \frac{1}{M_B} \right) \right]^{1/2}. \quad (2-11)$$

This means that as the gas flow rate, reactor pressure, or reactant concentration changes, the growth rate will change dramatically (Pierson 1992, Holstein 1992, Park 2001). Typically, the growth rate increases linearly with (1) the square root of the increasing forced flow parameter (a) (which is proportional to the overall gas flow velocity (a)), (2) the reagent gas phase mole fraction (y_A), and (3) the inverse of the pressure (Pierson 1992). These parameters can be used to reduce the boundary layer thickness such that reagent transport to the substrate and by-product transport away from the substrate is rapid (Pierson 1992, Dandy *et al.* 1995, Holstein 1992).

It should be noted that the growth rate depends on temperature in the mass-transfer limited regime. On one hand, the growth rate can increase slightly with increasing temperature (Eq. (2-11)). This is due to the increased diffusivity of reactants to the substrate (Huang 2003). (According to Huang, the dependence of the growth rate with temperature was scaled approximately to $T^{1.7}$ (2003).) On the other hand, the

growth rate can slightly decrease with increasing temperature. This is due to depletion of precursors within the gas phase directly above the substrate (Pulver *et al.* 2000, Pierson 1992). The precursors react above the substrate because of increased radiative heat transfer to the gas phase from the susceptor as the susceptor is heated to higher temperatures. The paragraphs to follow discuss the influence of these parameters on the growth rate of metal oxide formation.

Using the RWGSR to deposit zirconia below 1000°C was surface-reaction limited. Minet *et al.* determined that the CVD of zirconia in the $\text{ZrCl}_4\text{-H}_2\text{-CO}_2\text{-Ar}$ system had an exponential dependence on temperature (increased from $10^{-3} \mu\text{m h}^{-1}$ to approximately $1 \mu\text{m h}^{-1}$ from 900 to 1000°C) which was evident by the relatively high activation energy reported in this work ($E_a = 418 \text{ kJ mol}^{-1}$) (1987). This value was close to the activation energy of Brennfleck *et al.* (1981) ($E_a = 360 \text{ kJ mol}^{-1}$) from 860 to 900°C in zirconia CVD (Minet *et al.* 1987).

From 1000 to 1250°C, the formation of zirconia using the RWGSR was seen to depend on both the gas flow and temperature. On one hand, Sipp *et al.* (1992a) obtained a lower activation energy ($E_a = 40 \text{ kJ mol}^{-1}$) compared with that of Minet *et al.* (1987) ($E_a = 418 \text{ kJ mol}^{-1}$). Similarly, a lower activation energy (33 kJ mol^{-1} , from 1000°C to 1100°C) was reported by Wahl *et al.* in their deposition of zirconia using direct reaction with O_2 and ZrCl_4 . On the other hand, the growth rate increased linearly with increasing gas flow (by $0.83 \mu\text{m h}^{-1}$ from 300 to 1400 sccm), but there was no maximum growth rate reached above 1400 sccm (Sipp *et al.* 1992a).

Although the results above prompted Sipp *et al.* (1992a) to suggest that the rate-limited mechanism was either H_2 , CO_2 , or H_2O transport-limited or H_2O surface-

formation limited, it is clear that it is mass-transfer limited. The lower activation energy coupled with the linear dependence of the growth rate on increasing gas flow suggested that this regime was mass-transfer limited. Further, the low activation energies (33 and 40 kJ mol⁻¹) reported by Wahl *et al.* 1979 and Sipp *et al.* (1992a), respectively, were below a minimum value (42 kJ mol⁻¹) for which the process was considered surface-reaction limited (Matsuzaki *et al.* 1999, Choi and Kim 1992). The lack of a plateau of the deposition rate with increasing gas flow also indicates that the growth rate is mass-transfer limited in the temperature regime..

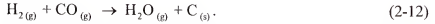
For yttria CVD in the YCl₃-H₂-CO₂-Ar system, Sipp *et al.* (1992b) found that the growth rate depended exponentially on temperature (increased from ~0.001 μm h⁻¹ to ~1 μm h⁻¹ from 1000 to 1100°C), with a reported activation energy of 616 kJ mol⁻¹. This activation energy, however, is not correct since it was miscalculated. The original work supported experimental data for the activation energy discussed previously, however, this activation energy is the mean of three activation energies reported in this work. These three activation energies (514, 538, and 765) were reported, however, with no experimental data and the mean should be 606 kJ mol⁻¹. Further, the reported experimental data were given for an E_a of 616 kJ mol⁻¹. An E_a of 606 kJ mol⁻¹ will be adopted for purposes of comparison in the remainder of this work. This relatively high activation energy value was not supported by Wahl (1979) (E_a = 406 kJ mol⁻¹ from 1000 to 1100°C) for yttria CVD from YCl₃ and O₂. Although these values do not agree, the high activation energy indicated that the process of yttria CVD using the RWGSR is surface-reaction limited below 1100°C.

For temperatures above 1100°C, no change was observed in the growth rate as a function of temperature, but the growth rate was linearly dependent on increasing gas flow (increased by approximately $15 \mu\text{m h}^{-1}$ from 300 to 1400 sccm). The change in dependency indicated a shift from the surface-reaction to the mass-transfer limited regime at $\sim 1100^\circ\text{C}$.

Although the apparent activation energy in the surface-reaction limited regime is an estimate, it is necessary to understand what this activation energy represents. Brennfleck *et al.* (1981) and Minet *et al.* (1987) obtained activation energies of 360 and 418 kJ mol^{-1} , respectively, in zirconia CVD. According to Minet *et al.* (1987), these values closely matched the activation energy of the RWGSR ($E_a = 325 \text{ kJ mol}^{-1}$ for the formation of H_2O and CO from 800 to 1000°C (Tingey 1966)). For yttria CVD, the activation energy (606 kJ mol^{-1}) obtained by Sipp *et al.* (1992b) disagreed with that of the RWGSR. Sipp *et al.* (1992b) do not offer any explanation as to why the activation energy is so large in comparison with the RWGSR. The large difference in the activation energies between Sipp *et al.* (1992b) and Tingey (1966), Minet *et al.* (1987) and Brennfleck (1981) was probably due to a step in the overall mechanism to oxidize yttrium that was limited by the surface temperature.

Although the results of zirconia CVD were promising, an issue arose concerning solid carbon ($\text{C}_{(s)}$) formation. Carbon is detrimental to the film quality and growth rate of zirconia films (Minet *et al.* 1987). Minet *et al.* (1987) obtained small amounts of $\text{C}_{(s)}$ (about 0.1 to 1 % of graphite by mass compared to zirconia) in zirconia films deposited at a temperature below 1000°C . They attributed this $\text{C}_{(s)}$ formation to excess inlet H_2 relative to inlet CO_2 (H_2/CO_2 molar ratio greater than unity) in the gas phase. Minet *et al.*

(1987) explained that excess hydrogen not only reduced CO_2 to CO and H_2O from the RWGSR (Eq. (2-5)), the remaining hydrogen further reduced CO to form an additional mole of water and solid carbon,



$\text{C}_{(s)}$, however, was not present when using the RWGSR in zirconia deposition above 1000°C and never present in yttria deposition (Sipp *et al.* 1992a, 1992b). In comparing the results of these three studies, it was apparent that the increased temperature and yttria presence limited carbon formation. This bodes well for YSZ CVD, and is necessary to determine if carbon formation is an issue.

The last experimental issue that arose was the amount of oxygen needed to carry out the deposition effectively. Sipp *et al.* (1992b) found that molar oxygen (n_O) to molar yttrium (n_Y) ratio (n_O / n_Y) of at least 18 ensured yttria CVD; otherwise, YOC was favored to deposit. Similarly, Minet *et al.* (1986) found that the molar oxygen to molar zirconium (n_Z) ratio (n_O / n_Z) of at least 4 ensured pure oxide formation of zirconia; otherwise, carbon formation occurred. Thus, it is reasonable to assume that the molar oxygen to molar yttrium and molar zirconium ratio ($n_O / (n_Y + n_Z)$) is between the n_O / n_Y and n_O / n_Z ratios and is necessary to ensure pure oxide formation of tetragonal YSZ. This relatively high oxygen content ensures that the precursors are fully oxidized.

2.7.3 Metal-Organic CVD (MOCVD) of YSZ

Differing from chloride CVD, metal-organic CVD (MOCVD) involves the reaction of metal-organic precursors onto a substrate to form the metal oxide coatings. In the case of refractory ceramics like YSZ, formation is dependent on reaction of the precursor with an oxidation source at moderate to high substrate temperature (500-

1000°C). Direct reaction of the metal-organic precursors with molecular oxygen has shown the potential to achieve the desired coating quality (Wahl *et al.* 2001a), thus, oxygen sources, such as water vapor and the RWGSR, were not studied for MOCVD in this work.

The MOCVD method has several important criteria that make it commercially viable. (Jones and Chalker 2003) First, the precursors must be efficiently volatilized and transported from the source zone to the reaction zone. Next, the deposition temperature “window” must be large. This large temperature window allows the precursors to decompose near the substrate so that precursor utilization is high. Finally, the deposited coatings must be of high purity and meet the materials needs of the application. Thus, precursor and oxygen source selection are vital to meeting these criteria. (Jones and Chalker 2003)

MOCVD encompasses a myriad of precursors; however, not all are suitable for deposition of YSZ TBCs. For example, precursors such as metal-alkylamides, metal-aryls and metal alkyls are suitable for slow growth rate ($< 0.1 \mu\text{m h}^{-1}$) metal nitride or metal carbide processes (Jones and Chalker 2003, Healy and Smith 1995, Berndt *et al.* 1995, Hanko *et al.* 1995, Parmeter *et al.* 1994).

Oxygenated β -diketonate precursors, such as $\text{Y}(\text{acac})_3$ $\text{Zr}(\text{acac})_4$ ($\text{acac} = \text{CH}_3\text{-C(=O)-CH}_2\text{-C(=O)-CH}_3$) were faster growing ($\sim 1 \mu\text{m h}^{-1}$), yet, were inadequate for TBC applications (Nubian *et al.* 2000, Matsuzaki *et al.* 1999). $\text{Y}(\text{acac})_3$ and $\text{Zr}(\text{acac})_4$ precursors had a volatilization temperature (160°C) very close to their decomposition temperatures (170 – 200°C) and growth temperatures (300 – 350°C) (Nubian *et al.* 2000). This close proximity of volatilization, decomposition, and growth temperatures made the

deposition window very small for coating growth. Further, the low growth temperatures caused the growth rates to be low, which made these precursors difficult to use (Nubian *et al.* 2000).

$\text{Y}(\text{octylate})_3$ and $\text{Zr}(\text{octylate})_4$ (octylate = $\text{C}_4\text{H}_9\text{-CH}(\text{CH}_2\text{-CH}_3)\text{-C(=O)-O}$) β -diketonate precursors were advantageous because they had higher decomposition temperatures (314°C and 326°C, respectively) and higher growth temperatures (550 – 750°C) (Matsuzaki *et al.* 1999). Yet, these precursors had low growth rates ($\sim 4 \mu\text{m h}^{-1}$) (Matsuzaki *et al.* 1999). The low growth rates were attributed to the low solution concentration (0.0045 M Y and 0.024 M Zr) of these precursors in their carrier solvent (toluene) (Matsuzaki *et al.* 1999). This low solubility meant that the gas phase mole fraction was low. This was disadvantageous in the mass-transfer limited regime since the deposition rate was linearly dependent on the reagent mole fraction and transport to the substrate (Pierson 1992).

The $\text{Y}(\text{tmhd})_3$ and $\text{Zr}(\text{tmhd})_4$ (tmhd = $\text{C(CH}_3)_2\text{-C(=O)-CH}_2\text{-C(=O)-C(CH}_3)_2\text{-CH}_3$) β -diketonate precursors showed promise as possible reagent candidates. Their favorability was due to their large difference in volatilization and growth temperatures ($T_{\text{growth}} - T_{\text{volatilization}} > 200^\circ\text{C}$), yielding a larger temperature window for deposition without the additional concern of precursor depletion in the gas phase (Pulver *et al.* 2000, Jones and Chalker 2003). Further, these precursors demonstrated high solubility in most industrial solvents (such as tetrahydrofuran, alcohols, and glyme) (Hubert-Pfalzgraf and Guillon 1998). Moreover, these precursors have demonstrated higher conversion efficiency ($> 35\%$) from metal-organic source to metal oxide coating (Tu *et al.* 2002, Wahl *et al.* 2001a, Wahl *et al.* 2001b, Kim *et al.* 2002). Growth rates

using these precursors ranged between 10 (Pulver *et al.* 2000) to 50 $\mu\text{m h}^{-1}$ (Wahl *et al.* 2001a).

Lower-cost alkoxide precursors (with small ligands such as OPr^i , OPr^n , OBut^i , or OBut^n ligands) had comparable vaporization temperatures as $\text{Y}(\text{tmhd})_3$ and $\text{Zr}(\text{tmhd})_4$ precursors. Further, the alkoxy ligand contributed less carbon per mole of metal atom as compared to $\text{Y}(\text{tmhd})_3$ and $\text{Zr}(\text{tmhd})_4$ precursors, suggesting that high purity coatings are obtained with possibly less oxygen. Insufficient growth rates, however, using the $\text{Zr}(\text{OPr}^i)_4$ ($\text{OPr}^i = \text{O-CH}(\text{CH}_3)_2$) ($\sim 2.2 \mu\text{m h}^{-1}$) and $\text{Zr}(\text{OPr}^n)_4$ ($\text{OPr}^n = \text{O-CH}_2\text{-CH}_2\text{-CH}_3$) ($\sim 0.5 \mu\text{m h}^{-1}$) precursors were observed, which made these precursors unsuitable for TBC fabrication (Krumdieck *et al.* 2002, Yoshikawa 2002). The low growth rates were due to the poor solubility and evaporation of $\text{Zr}(\text{OPr}^i)_4$ in a toluene carrier solvent and the $\text{Zr}(\text{OPr}^n)_4$ vapor pressure (0.1 torr at 208°C) and low overall gas flow rate ($200 \text{ cm}^3 \text{ min}^{-1}$) for deposition in the mass-transfer limited regime (Krumdieck *et al.* 2002, Yoshikawa 2002).

Precursors with butoxyl ligands showed mixed results. On one hand, (Burlescon *et al.* 2002, Cameron and George 2001, Chang *et al.* 2001) attempted zirconia growth using $\text{Zr}(\text{OBut}^i)_4$ ($\text{OBut}^i = \text{O-C}(\text{CH}_3)_3$) and yielded low growth rates (0.6, 0.5, and 2.4 $\mu\text{m h}^{-1}$, respectively). The low growth rates were due to the low vapor pressure (~ 0.45 torr at 250°C) and the use of a high vacuum reaction chamber in which molecular interactions were less frequent. Further, it was seen that the carbon content increased from 2.8 wt. % to 13.8 wt. % as the growth temperature increased from 400°C to 500°C due to the decreasing zirconia growth rate with increasing temperature. Both observations were

made due to the close matching of the decomposition temperature and the vaporization temperature for $\text{Zr}(\text{OBut}^t)_4$ (Chour *et al.* 1997).

On the other hand, growth rates as high as $8.9 \mu\text{m h}^{-1}$ were achieved using the $\text{Zr}(\text{OBut}^n)_4$ precursors (Chour *et al.* 1997). This was due to the use of water vapor to assist in precursor reaction at the substrate (Chour *et al.* 1997). Of note with the work of Chour *et al.* 1997 is the use of a 0.4 M $\text{Zr}(\text{OBut}^n)_4$ -*n*-butanol precursor solution for MOCVD. Recently, Aldrich Chemicals, Inc. improved the solubility of this precursor solution to 2.23 M and has also introduced a 0.5 M $\text{Y}(\text{OBut}^n)_3$ -toluene precursor solution. This shows the potential for increasing the growth rate for deposition in the mass-transfer limited regime. Thus, two MOCVD precursors were used in this work: β -diketonate ($\text{Y}(\text{tmhd})_3$ with $\text{Zr}(\text{tmhd})_4$) and alkoxide ($\text{Y}(\text{OBut}^n)_3$ with $\text{Zr}(\text{OBut}^n)_4$). The research efforts to fabricate YSZ with these precursors are summarized in Table 2-2 and are discussed below.

Finally, the choice of an oxygen source is important for ensuring high quality coating growth. According to Chiang *et al.* (1992) and Igumenov *et al.* (2001), additional oxidant (such as O_2 or H_2O) can minimize carbon formation during growth of metal oxide thin films using metal- β -diketonate precursors. These authors suggested that metal- β -diketonate decomposition on the surface led to incomplete decomposition of the β -diketonate organic ligand, thus trapping carbon in the growing film. The addition of an oxidant allowed the carbon to combine with the available oxygen atoms and desorb from the surface as a volatile compound (such as CO or CO_2) (Chiang *et al.* 1992, Igumenov *et al.* 2001).

Further, Chiang *et al.* (1992) and Igumenov *et al.* (2001) suggested that additional oxidant lowered the surface-reaction limited temperature range while using metal- β -diketonate precursors. Normally, surface-reaction intermediates formed at relatively high temperatures ($> 700^{\circ}\text{C}$) without the presence of water vapor (Chiang *et al.* 1992) or O_2 (Igumenov *et al.* 2001). When water vapor or oxygen was added, the temperature range for surface-reaction limited growth decreased (by as much as 200°C) due to the formation of the same surface reaction intermediates at lower temperatures (Chiang *et al.* 1992, Igumenov *et al.* 2001). This lowering of the surface-reaction limited temperature range is advantageous since coating growth rate optimization in the mass-transfer limited regime can be performed at lower temperatures. Further, it is reasonable to assume that the addition of an oxidant can enhance the growth for metal-*n*-butoxide precursors. Thus, an additional oxygen source will be used in this work to enhance deposition quality and growth rate.

2.7.4 Parameters Influencing MOCVD Growth Rates

The parameters influencing MOCVD using $\text{Y}(\text{tmhd})_3$ and $\text{Zr}(\text{tmhd})_4$ and $\text{Y}(\text{OBut}^n)_3$ and $\text{Zr}(\text{OBut}^n)_4$ precursors followed those discussed for metal chloride CVD..

For YSZ deposition using $\text{Y}(\text{tmhd})_3$ and $\text{Zr}(\text{tmhd})_4$ precursors, the growth rate was surface-reaction limited below 740 to 770°C . This surface-reaction limited regime was indicated by the exponential dependence of the growth rate on surface temperature. For example, Dubourdieu *et al.* (1999) obtained a growth rate of $0.018 \mu\text{m h}^{-1}$ at 400°C . When the temperature was increased to 500°C , they estimated the growth rate to be $0.18 \mu\text{m h}^{-1}$, with an $E_a = 160 \text{ kJ mol}^{-1}$ (Dubourdieu *et al.* 1999). Similar results were given by Kim *et al.* (2002), and Pulver *et al.* 2000) with good agreement in E_a amongst these

workers. (Although growth data for Pulver *et al.* (2000)) is given for zirconia CVD, the general trends in the growth were useful to this discussion).

It is important to understand what E_a for MOCVD processes signified. Pulver *et al.* (2000) and Dubourdieu *et al.* (1999) offered that this E_a is indicative of the thermal activation for metal adsorption onto the substrate and the corresponding metal-organic and organic reaction products desorbing from the substrate surface. In comparison with the E_a (360-418 kJ mol⁻¹) for chloride CVD using the RWGSR, it was apparent that the E_a (≤ 160 kJ mol⁻¹) for MOCVD processes (Table 2-2) were lower than those of chloride CVD processes (discussed above). Based on this data, it appears that the metal adsorption and reaction by-product desorption during MOCVD was relatively fast as compared to surface water molecule formation while using the RWGSR as an oxygen source during chloride CVD.

The mass-transfer limited regime was observed for temperatures higher than 740–770°C (Chevalier *et al.* 2003, Dubourdieu *et al.* 1999, Kim *et al.* 2002, Martinez *et al.* 1998, Jun *et al.* 2003). The growth rate in this regime approached a maximum at approximately 740-830°C (Dubourdieu *et al.* 1999, Kim *et al.* 2002, Chevalier *et al.* 2003) and reached a plateau (Kim *et al.* 2002) or decreased with increasing temperature (Pulver *et al.* 2000). The slight decreased growth rate with increasing temperature was attributed to gas-phase precursor depletion and the formation of homogeneously nucleated particles of YSZ (Pulver *et al.* 2000).

Previous work using Y(tmhd)₃ and Zr(tmhd)₄ illustrated other parameters with significant effect on CVD of YSZ, yttria, and zirconia. Dubourdieu *et al.* (2000) also demonstrated that the growth rate was linearly dependent on the precursor feed rate

(Table 2.2). Using the displacement of a screw motor, (in cm min^{-1}) that precisely delivered a powder precursor mixture of $\text{Y}(\text{tmhd})_3$ and $\text{Zr}(\text{tmhd})_4$, Dubourdieu *et al.* (2000) showed that the growth rate increased from $3.9 \mu\text{m h}^{-1}$ (0.14 cm min^{-1}) to $39 \mu\text{m h}^{-1}$ (1.4 cm min^{-1}). Pulver *et al.* (2000) demonstrated that the dependence of the growth rate was quadratic with respect to the vapor phase mole fraction (y) of $\text{Zr}(\text{tmhd})_4$ ($y_{\text{Zr}(\text{tmhd})_4}$). They obtained growth rates (at 700°C and $y_{\text{O}_2} = 0.167$) of 10, 60, and $63 \mu\text{m h}^{-1}$ at $y_{\text{Zr}(\text{tmhd})_4}$ of 0.0025, 0.018, and 0.024, respectively (Pulver *et al.* 2000). Their results were obtained using a hot-wall CVD reactor, however, in which precursor depletion occurred at relatively high precursor vapor phase mole fractions (Park 2001).

Although there is a wealth of literature on the use of $\text{Zr}(\text{OBut}^n)_4$, for ZrO_2 formation (Maggio *et al.* 1995, Maggio *et al.* 1997, Maggio *et al.* 1998, Hu *et al.* 2000), only Chour *et al.* studied this precursor's role in MOCVD of YSZ (1997). For the yttrium source, they used $\text{Y}(\text{tmhd})_3$ (Chour *et al.* 1997). The surface-reaction limited regime was indicated by an increase in the growth rate from $0.44 \mu\text{m h}^{-1}$ at 400°C to $8.9 \mu\text{m h}^{-1}$ at 700°C with an E_a of 45.5 kJ mol^{-1} . This activation energy represents the reaction of these precursors in flowing O_2 that had been humidified to hasten the surface-reaction pathway (Chour *et al.* 1997). In comparison, $\text{Si}(\text{OBut}^n)_4$ in flowing O_2 (without water vapor) yielded an $E_a = 125\text{-}170 \text{ kJ mol}^{-1}$, which showed the effect of using water vapor to assist in precursor reaction (Chour *et al.* 1997).

A consequence of employing MOCVD was the possibility of carbon contamination. Carbon contamination was an issue since the precursor molecules have a high carbon to metal ratio. Ideally, carbon atoms remain attached to the organic ligand as it is swept away after precursor reaction on the substrate, however, this is usually not the

case. In the thermodynamic literature, it was found that high temperatures, low pressures, and excess oxygen content helped to eliminate carbon formation (Frederickson *et al.* 1996). In their YSZ experiments, Chevalier *et al.* attributed the formation of carbon to the incomplete decomposition of the precursor ligand on the substrate surface (2003). The formation of carbon appeared only on the surface of the coating (Chevalier *et al.* 2003) and was eliminated by a post-deposition high temperature ($\sim 1000^{\circ}\text{C}$) heat treatment of the sample in air. Nevertheless, steps were taken in this work to minimize and possibly avoid carbon formation.

Table 2-1. Investigation of chloride CVD for ZrO_2 , Y_2O_3 , and YSZ

Reference	Substance	Description of Investigation	Initial conditions
Minet <i>et al.</i> (1986)	Zirconia	Thermodynamic study	$727^{\circ}\text{C} \leq T \leq 1227^{\circ}\text{C}$
		Oxidant: H_2 , CO_2	$P \leq 0.5$ bar
		Diluent gas: Ar	0.01
		Precursors: ZrCl_4	$\leq P^0_{\text{H}_2}/P^0_{\text{CO}_2} \leq 1000$ $0.001 \leq P^0_{\text{ZrCl}_4}/P \leq 1$
Results:			
a. Pure, monoclinic zirconia was thermodynamically stable at these initial conditions.			
b. The yield of carbon decreased as overall pressure was increased.			
c. Deposition of zirconia and carbon decreased with increasing temperature above 827°C . Deposition of zirconia and carbon increased with decreasing temperature below 827°C .			
d. When H_2/CO_2 is less than unity, pure zirconia deposits. When H_2/CO_2 is greater than unity, both zirconia and carbon deposit.			
$P^0_{\text{ZrCl}_4}$ is the partial pressure of ZrCl_4 , $P^0_{\text{H}_2}$ is the partial pressure of H_2 , $P^0_{\text{CO}_2}$ is the partial pressure of CO_2			
Minet <i>et al.</i> (1987)	Zirconia	Experimental study	$800^{\circ}\text{C} \leq T \leq 1000^{\circ}\text{C}$
		Oxidant: H_2 , CO_2	$0.0197 \text{ bar} \leq P \leq 0.0987$ bar
		Diluent gas: Ar	$0.3 \leq P^0_{\text{H}_2}/P \leq 0.6$
		Precursors: ZrCl_4	$1 \leq P^0_{\text{H}_2}/P^0_{\text{CO}_2} \leq 3$ $0.01 \leq P^0_{\text{ZrCl}_4}/P \leq 0.02$

Results:

- From XRD, monoclinic zirconia deposited with carbon at these initial conditions.
- As overall pressure was increased, carbon yield decreased.
- As temperature increased, carbon yield increased. As temperature decreased, carbon yield decreased.
- When α was greater than unity, carbon yield decreased

Table 2-1. Continued

Reference	Substance	Description of Investigation	Initial conditions
Sipp <i>et al.</i> (1992a)	Zirconia		$950^{\circ}\text{C} \leq T \leq 1550^{\circ}\text{C}$
		Experimental study	$0.0197 \text{ bar} \leq P \leq 0.0494 \text{ bar}$
		Oxidant: H_2 , CO_2	$0.04 \leq P^{\circ}_{\text{H}_2}/P \leq 0.2$
		Diluent gas: Ar	$P^{\circ}_{\text{H}_2}/P^{\circ}_{\text{CO}_2} = 3$
		Precursors: ZrCl_4	$0.0025 \leq P^{\circ}_{\text{ZrCl}_4}/P \leq 0.0123$

Results:

- From Arrhenius plots, tetragonal zirconia deposited; however, no characterization was done to show the presence of carbon at these initial conditions.
- As overall pressure increased, zirconia yield increased.
- As temperature increased, zirconia yield increased.
- As overall gas concentration increased, zirconia yield increased.

Sipp <i>et al.</i> (1992b)	Yttria		$1000^{\circ}\text{C} \leq T \leq 1300^{\circ}\text{C}$
		Experimental study	$0.00494 \text{ bar} \leq P \leq 0.0494 \text{ bar}$
		Oxidant: H_2 , CO_2	$0.04 \leq P^{\circ}_{\text{H}_2}/P \leq 0.2$
		Diluent gas: Ar	$P^{\circ}_{\text{H}_2}/P^{\circ}_{\text{CO}_2} = 3$
		Precursor: YCl_3	$0.00667 \leq P^{\circ}_{\text{YCl}_3}/P \leq 0.0133$

Results:

- From XRD, cubic yttria deposited with no carbon and some YOCl at these initial conditions.
- As overall pressure was increased, cubic yttria yield was 100%.
- As temperature increased, cubic yttria yield increased. As temperature decreased, YOCl yield increased.
When $\beta = ([\text{CO}_2]/[\text{YCl}_3])$ was greater than nine, cubic yttria yield 100%. Otherwise YOCl was the major deposited phase.

Table 2-1. Continued

Reference	Substance	Description of Investigation	Initial conditions
Yamane and Harai (1989)	YSZ	Experimental study	$110^{\circ}\text{C} \leq T \leq 1200^{\circ}\text{C}$
		Oxidant: O_2	$P = 1 \text{ bar}$
		Diluent gas: Ar	$P^{\circ}_{\text{O}_2}/P \leq 0.45$
		Precursor: ZrCl_4 , YCl_3	$0.25 \leq P^{\circ}_{\text{YCl}_3}/P^{\circ}_{\text{ZrCl}_4} \leq 1.5$
Results			
a. From XRD, cubic YSZ deposited at these initial conditions.			
Determined that the mole fraction of yttria in YSZ was a linear function of $x = P^{\circ}_{\text{YCl}_3}/(P^{\circ}_{\text{YCl}_3} + P^{\circ}_{\text{ZrCl}_4})$.			
Cao <i>et al.</i> (1993)	YSZ	Experimental study	$800^{\circ}\text{C} \leq T \leq 1000^{\circ}\text{C}$
		Oxidant: H_2O	$P = 0.00197 \text{ bar}$
		Diluent gas: Ar	$P^{\circ}_{\text{H}_2\text{O}}/P = 0.75 \text{ bar}$
		Precursors: ZrCl_4 , YCl_3	$P^{\circ}_{\text{ZrCl}_4}/P^{\circ}_{\text{YCl}_3} = 3.33$
Results:			
From XRD, cubic YSZ deposited at these conditions.			

Table 2-2. Investigation of MOCVD of ZrO_2 , Y_2O_3 , and YSZ using $\text{Y}(\text{tmhd})_3$ and $\text{Zr}(\text{tmhd})_4$ and $\text{Zr}(\text{OBut}^n)_4$

Reference	Substance	Description of Investigation	Initial Conditions
Kim <i>et al.</i> (2002)	YSZ	Experimental Sublimation of $\text{Zr}(\text{tmhd})_4$ and $\text{Y}(\text{tmhd})_3$	$700 < T(^{\circ}\text{C}) < 800$
			$P_{\text{total}} = 530 \text{ Pa}$
			$\dot{Q}_{\text{total}} = 900 \text{ ml min}^{-1}$
			$y_{\text{O}_2} = 0.33$
			$y_{\text{Zr}(\text{tmhd})_4} + y_{\text{Y}(\text{tmhd})_3} = 6.2 \cdot 10^{-5}$
			$\frac{y_{\text{Y}(\text{tmhd})_3}}{y_{\text{Zr}(\text{tmhd})_4} + y_{\text{Y}(\text{tmhd})_3}} = 0.16$

Results:

- YSZ surface-kinetic limited regime: $0.109 \mu\text{m h}^{-1}$ to $1.5 \mu\text{m h}^{-1}$ ($700\text{--}770^{\circ}\text{C}$)
 - $E_a = 152 \pm 7 \text{ kJ mol}^{-1}$.
- Mass transfer limited regime: $1.5 \mu\text{m h}^{-1}$ (770) to $1.5 \mu\text{m h}^{-1}$ (800).

Chevalier <i>et al.</i> (2003)	YSZ	Experimental Sublimation of Zr(tmhd) ₄ and Y(tmhd) ₃ precursors, carried by N ₂ , reacted with O ₂	T(°C) = 750
			P _{total} = 5300 Pa
			Q̇ _{total} = 600 ml min ⁻¹
			y _{O₂} = 0.5
			T ^{Zr(tmhd)₄} _{sublimation} (°C) = 180
			125 < T ^{Y(tmhd)₃} _{sublimation} (°C) < 150

Results:

- Growth rate between 0.3 to $0.4 \mu\text{m h}^{-1}$.
- Yttria content (from 2.5 to $17.6 \text{ at.}\%$) was found to be linear with $T_{\text{sublimation}}^{\text{Y}(\text{tmhd})_3}$.
- 2.5 , 5.6 , and $7.9 \text{ at.}\%$ YSZ film was tetragonal, $7.9 \text{ at.}\%$ YSZ films were cubic.

Table 2-2. Continued

Reference	Substance	Description of Investigation	Initial Conditions
Chour <i>et al.</i> (1997)	YSZ	Experimental Sublimation of Zr(OBut ⁿ) ₄ and Y(tmhd) ₃	400 < T(°C) < 840
			P _{total} = 8000 Pa
			y _{H2O} + y _{air} = 0.82
			y _{Y(tmhd)₃ + Zr(tmhd)₄ + O₂} = 0.18
			$\frac{y_{Y(tmhd)_3}}{y_{Y(tmhd)_3} + y_{Zr(tmhd)_4}} = 0.19$

Results:

- maximum growth rate of $8.9 \mu\text{m h}^{-1}$ at 840°C .
- surface-reaction limited regime: $0.44 \mu\text{m h}^{-1}$ (400°C) to $8.9 \mu\text{m h}^{-1}$ (840°C).
- obtained 5 mol% Y_2O_3 - ZrO_2 films.
- (111) slightly preferred orientation (cubic YSZ)

Pulver <i>et al.</i> (2000)	ZrO ₂ , Y ₂ O ₃ , YSZ	Experimental Sublimation of Zr(tmhd) ₄ and Y(tmhd) ₃ precursors	480 < T(°C) < 740
			P _{total} = 1000 Pa
			Q _{total} = 250 ml min ⁻¹
			y _{O₂} = 0 or 0.67
			0 < y _{Zr(tmhd)₄} < 0.05
			0 < y _{Y(tmhd)₃} < 0.05

Results:

- ZrO_2 max. growth rate of $20 \mu\text{m h}^{-1}$ at 640°C ($y_{\text{Zr(tmhd)}_4} = 0.001$, $y_{\text{O}_2} = 0.167$)
- ZrO_2 surface-reaction limited regime: $1.2 \mu\text{m h}^{-1}$ (540°C) to $12 \mu\text{m h}^{-1}$ (610°C), $E_a \approx 104 \text{ kJ mol}^{-1}$.
- Y_2O_3 surface-reaction limited regime: $E_a = 126 \text{ kJ mol}^{-1}$.
- YSZ maximum growth rate of $50 \mu\text{m h}^{-1}$.

Jun <i>et al.</i> (2003)	YSZ	Experimental Liquid-Injection of Zr(tmhd) ₄ and Y(tmhd) ₃ precursors	$660 < T(^{\circ}\text{C}) < 800$
			$P_{\text{total}} = 1330 \text{ Pa}$
			$100 < Q_{\text{O}_2} (\text{ml min}^{-1}) < 500$

Results:

- Y:Zr solution molar ratio of 0.2:0.8 in tetrahydrofuran solvent.
- Maximum growth rate of $6 \mu\text{m h}^{-1}$ at 740°C and $Q_{\text{O}_2} = 300 \text{ sccm}$.

Table 2-2. Continued

Reference	Substance	Description of Investigation	Initial Conditions
Fredricksson <i>et al.</i> (1996)	ZrO ₂	Thermodynamic calculation using ERVICALC for Zr(tmhd) ₄ , O ₂ , and Ar	$0 < T(^{\circ}\text{C}) < 1000$ $P_{\text{total}} = 133, 1330, \text{ and } 13300 \text{ Pa}$ $0 < \omega = \frac{n_{\text{O}_2}}{n_{\text{Zr(tmhd)}_4} + n_{\text{O}_2} + n_{\text{Ar}}} < 0.8$
Results:			
a. Pure zirconia deposition favored for $T > 600^{\circ}\text{C}$, $P < 133 \text{ Pa}$, and $\omega > 0.25$.			
b. Carbon deposition favored for $T < 600^{\circ}\text{C}$, $P > 133 \text{ Pa}$, and $\omega < 0.25$.			
Martinez <i>et al.</i> (1998)	YSZ	Experimental Sublimation of Zr(tmhd) ₄ and Y(tmhd) ₃ precursors, carried by Ar, reacted with O ₂	$T(^{\circ}\text{C}) = 690$ $P_{\text{total}} = 670 \text{ Pa}$ $\dot{Q}_{\text{total}} = 350 \text{ ml min}^{-1}$ $y_{\text{O}_2} = 0.14$ $T_{\text{sublimation}}^{\text{Zr(tmhd)}_4} (^{\circ}\text{C}) = 160$ $125 < T_{\text{sublimation}}^{\text{Y(tmhd)}_3} (^{\circ}\text{C}) < 135$
Results:			
a. Lattice parameter calculation showed that 8-10 mol% YSZ formed.			
b. Cubic YSZ formed (no growth rate given).			
Dubourdieu <i>et al.</i> (1999)	YSZ	Experimental Elaborate solid precursor delivery of Zr(tmhd) ₄ and Y(tmhd) ₃ , carried by Ar, reacted with O ₂	$T_{\text{substrate}} (^{\circ}\text{C}) = 450-800$ $P_{\text{total}} = 400 \text{ Pa}$ $\dot{Q}_{\text{O}_2, \text{N}_2, \text{O}} = 100-200 \text{ ml min}^{-1}$ $\dot{Q}_{\text{Ar}} = 50-200 \text{ ml min}^{-1}$ $\dot{Q}_{\text{Zr(tmhd)}_4, \text{Y(tmhd)}_3} = 0.0075-1.35 \text{ ml min}^{-1}$ $T_{\text{sublimation}}^{\text{Zr(tmhd)}_4, \text{Y(tmhd)}_3} (^{\circ}\text{C}) = 300-350$
Results:			
a. Maximum growth rate of $42 \mu\text{m h}^{-1}$ at 830°C (horizontal reactor).			
b. Growth rate linearly dependent on precursor feed rate: $3.9 \mu\text{m h}^{-1}$ (0.14 cm min^{-1}) to $39 \mu\text{m h}^{-1}$ (1.4 cm min^{-1}).			
c. $E_a = 160 \text{ kJ mol}^{-1}$; $0.018 \mu\text{m h}^{-1}$ (435°C) to $0.18 \mu\text{m h}^{-1}$ (500°C).			
d. linear dependence of film yttria content with yttrium precursor concentration.			

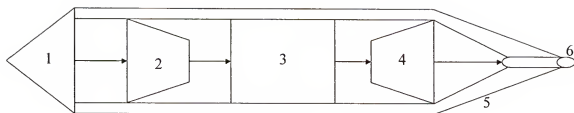


Figure 2-1. Cutout of an aircraft engine. Components: (1) intake fan, (2) compressor, (3) combustor, (4) turbine, (5) exhaust manifold, and (6) thrust nozzle.
Adapted from: Owen, N. H., W. F. O'Brien and J. T. Hamrick, Eds., "Basic Gas Turbine Engine Technology," International Gas Turbine Institute, Atlanta (1991).

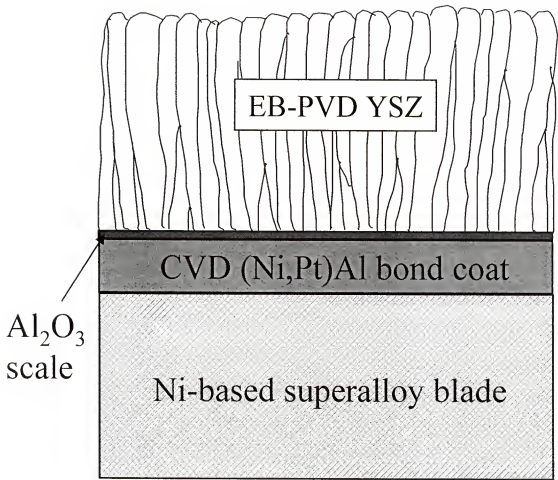


Figure 2-2. Schematic of the current state-of-the-art TBC system used in gas turbines. Adapted from: a) Haynes, J. A., *Oxidation and Degradation of Thermal Barrier Coating Systems*, Material Science and Engineering Department, University of Alabama, Tuscaloosa, AL (1997) and b) Clarke, D. R. and C. G. Levi, "Materials Design for the Next Generation Thermal Barrier Coatings," *Annual Review in Materials Research*, **33**, 383–417 (2003).

Figure 2-3. Experimental phase diagram of the $\text{YO}_{1.5}\text{-ZrO}_2$ system.
Adapted from: a) Stubican, V. S., "Phase Equilibria and Metastabilities in the Systems $\text{ZrO}_2\text{-MgO}$, $\text{ZrO}_2\text{-CaO}$, $\text{ZrO}_2\text{-Y}_2\text{O}_3$," *Science and Technology of Zirconia III*. N. Y. S. Somiya, H. Yanagida, **24A**, 71 (1988) and b) Suzuki, Y., "Phase Transition Temperature of Fluorite-type $\text{ZrO}_2\text{-Y}_2\text{O}_3$ Solid Solutions Containing 8-44 mol% Y_2O_3 ," *Solid State Ionic's*, **81**, 211 (1995).

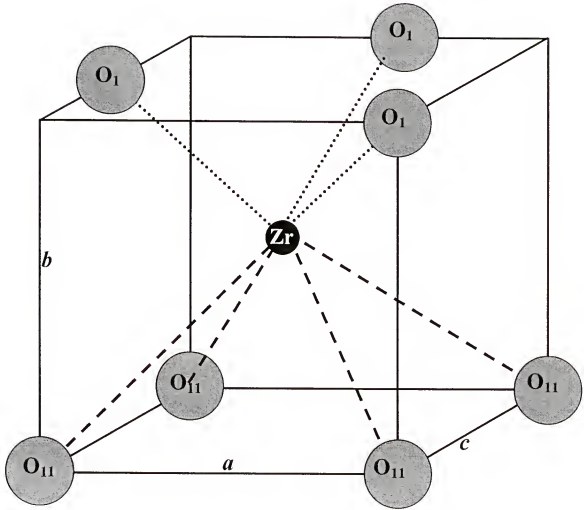


Figure 2-4. Schematic representation of monoclinic ZrO₂ crystal lattice. Lattice parameters (Å): $a = 5.156$, $b = 5.30$, $c = 5.191$. Average Zr-O₁₁ bond length = 2.21 Å, average Zr-O₁ bond length = 2.07 Å. The O₁₁ and O₁ designations were given for two different Zr-O bond lengths, however, these bond lengths are different for each Zr-O bond and are listed within the source. Adapted from: Subbarao, E. C., "Zirconia—An Overview," *Science and Technology of Zirconia*. A. H. Heuer and L. W. Hobbs, Columbus, American Ceramic Society, **3**, 1-13 (1981).

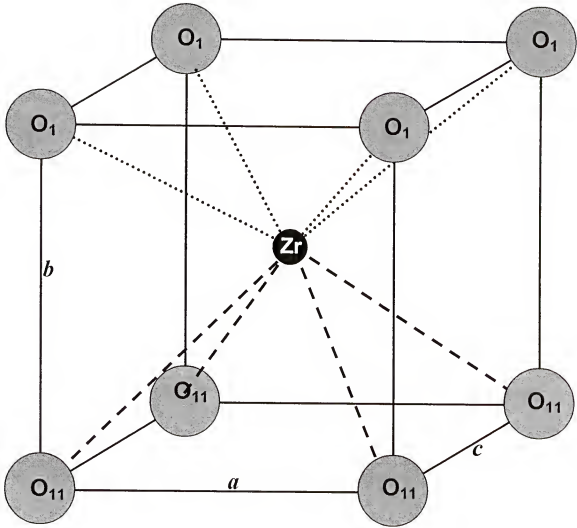


Figure 2-5. Schematic representation of the tetragonal ZrO_2 crystal lattice. Lattice parameters ($\text{\AA}$): $a = 5.094$, $b = 5.177$, $c = 5.094$. Average Zr-O11 bond length $2.445 \text{ \AA}$, average Zr-O1 bond length $= 2.065 \text{ \AA}$. The O₁₁ and O₁ designations were given for two different Zr-O bond lengths: Zr-O₁₁ has an average bond length of $2.455 \text{ \AA}$ and the Zr-O₁ has an average bond length of $2.065 \text{ \AA}$. Adapted from: Subbarao, E. C., "Zirconia—An Overview," *Science and Technology of Zirconia*. A. H. Heuer and L. W. Hobbs, Columbus, American Ceramic Society, 3, 1-13 (1981).

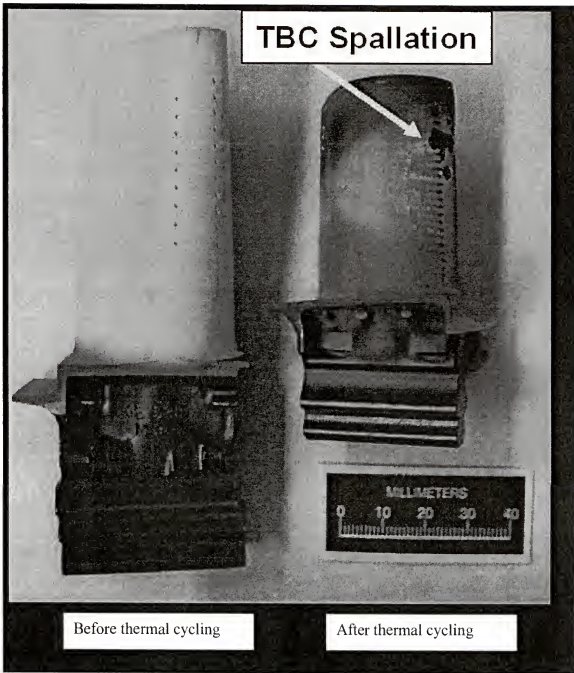


Figure 2-6. Effect of Engine Exposure on YSZ coated turbine blade. *Source:* Haynes, J. A., "TBCs," *Presentation*, University of Tennessee, Knoxville, TN, (2002).

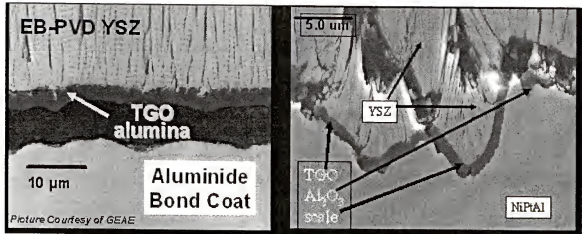


Figure 2-7. Comparison of delamination behavior of ceramic of cast NiAl bond coat (left) and ceramic delamination on CVD NiPtAl bond coat (right). *Source:* Haynes, J. A., "TBCs," *Presentation*, University of Tennessee, Knoxville, TN, (2002).

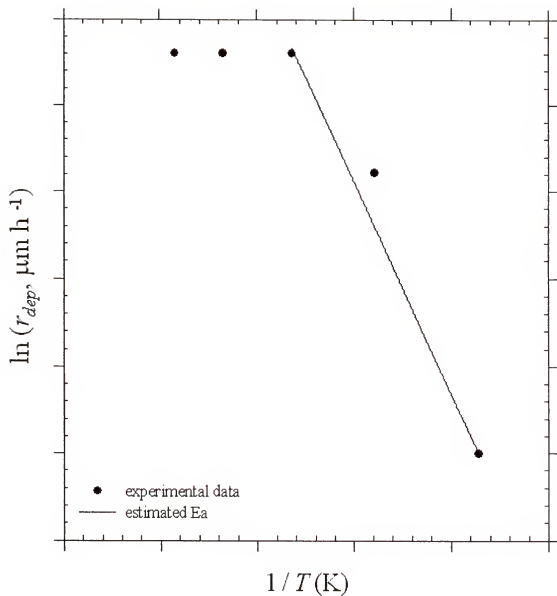


Figure 2-8. Example of Arrhenius plot with estimation of activation energy for sample experimental data. (Experimental data on this plot are arbitrary and are used only as an example.)

CHAPTER 3 EQUILIBRIUM MODELING

The results of equilibrium modeling are presented in this chapter. They include the results of calculation performed in both chloride and MOCVD. In chloride CVD, two subsystems (the Zr-Cl-O-C-H-Inert and Y-Zr-Cl-O-C-H-Inert systems) are investigated. In MOCVD (the Y-Zr-O-C-H system), one system is investigated, however, they are divided into two sets of precursors and their respective solvents. The results were presented and discussed below.

3.1 Thermochemical Properties

3.1.1 Pure Substances

Listed in Table 3-1 are the collected thermochemical properties for each element and pure substance that were considered beyond the existing ThermoCalc database. The information listed in this table is the standard enthalpy of formation at 298 K ($\Delta H_{f, 298}$), the heat capacity relations (C_p), and the standard entropy at 298 K (S_{298}^0). The heat capacity relation used in ThermoCalc is of the form

$$C_p = a + bT + cT^2 + \frac{d}{T^2}, \quad (3-1)$$

where T is the absolute temperature, and a , b , c , and d is fitted variables. Since this work focused on CVD at temperatures between 300°C and 1500°C, liquid species were not considered.

Thermochemical properties for gaseous YCl_3 were not given in standard compendia and were thus found from other literature sources. Pashinkin *et al.* (1952),

who used Knudsen cell mass spectrometry, reported an enthalpy of sublimation of $168.197 \pm 16.736 \text{ kJ mol}^{-1}$, which differed from the value of $297.1 \pm 8.8 \text{ kJ mol}^{-1}$ obtained from Barin (1989) and Kubaschewski *et al.* (1996), who also tabulated S^0_{298} and specific heat constants for $\text{YCl}_{3(g)}$. Other than these two data sources, no other data on YCl_3 gas were reported. The values from Kubaschewski *et al.* (1996) were used in this work.

3.1.2 Phase Diagram for the Zr-O System

The Zr-O computed phase diagram assessment by Liang *et al.* (2001) compared very well with the experimental phase diagram for the Zr-O system of Ondik and McMurdie (1998). Liang *et al.* (2001) employed experimental heat capacity and experimental phase diagram data in their assessment of the Zr-O system. These experimental heat capacity and phase diagram data were generated from various calorimetry studies, vapor pressure studies, x-ray diffraction studies, and electrical resistivity studies (Liang *et al.* 2001). The experimental phase diagram based on these data was reported by Ondik and McMurdie (1998) and is given in Figure 3-1

In their assessment, Liang *et al.* used a variety of models to describe the phase diagram information in the Zr-O system. (2001) First, they used the ideal gas model to describe the gas phase interactions of gas phase species. Second, the monoclinic zirconia (αZrO_2) and tetragonal zirconia (βZrO_2) phases were taken to be stoichiometric. Finally, the two-sublattice model was used to describe both the hexagonally close packed (hcp) zirconium (αZr) and body-centered cubic (bcc) zirconium (βZr). The two-sublattice model was used to describe αZr and βZr based on reported experimental data that showed ability for oxygen to be soluble in Zr in both of these crystalline phases (Liang *et*

al. 2001). The results of which are plotted for all oxygen compositions up to 1500°C in Figure 3-2.

The two-sublattice model describes the crystal lattice of a material phase where one sublattice is occupied by Zr and the other sublattice is occupied by the interstitial species. The interstitial species are a random mixture of O atoms and vacancies (Vac) thus giving the form $\text{Zr}(\text{O}, \text{Vac})_q$. The term, q , is the ratio of the interstitial sites to the lattice atoms and is unity for αZr and three for βZr (Liang *et al.* 2001).

The two-sublattice model formalism is given by

$$G_m^\phi - H^{SER} = \frac{1}{1 + qy_O} \left[{}^{me}G_m^\phi + {}^{id}G_m^\phi + {}^{ex}G_m^\phi \right], \quad (3-2)$$

where G_m^ϕ is the molar Gibbs energy of mixing for the solid solution phase (ϕ) (Liang *et al.* 2001). The first term on the right hand side of Eq. (3-2) represents the mole fraction (x) of zirconium atoms occupying interstitial sites in the lattice,

$$x_{\text{Zr}} = \frac{1}{1 + qy_O}. \quad (3-3)$$

In Eq. (3-3), y_O is the sublattice mole fraction (y) of oxygen atoms.

The second term on the right hand side of Eq.(3-2), ${}^{me}G_m^\phi$, is the molar Gibbs energy of the mechanical mixing (simple component mixing) of oxygen atoms and vacancies on the interstitial sublattice and is given by,

$${}^{me}G_m^\phi = y_O \left({}^oG_{\text{ZrO}}^\phi - H_{\text{Zr}}^{SER} - qH_O^{SER} \right) + y_{\text{Vac}} \left({}^oG_{\text{ZrVac}}^\phi - H_{\text{Zr}}^{SER} \right). \quad (3-4)$$

In Eq. (3-4), and ${}^oG_{\text{ZrO}}^\phi - H_{\text{Zr}}^{SER} - qH_O^{SER}$ is the molar Gibbs energy of the compound phase (αZrO_2 and βZrO_2) with all interstitial sites filled, H_{Zr}^{SER} and H_O^{SER} are the stable element reference enthalpies (at 298.15 K and 1 bar) of 1 mole of hcp Zr and a ½ mole of

O₂ gas, respectively, y_{Vac} is the sublattice mole fraction of vacancies, and ${}^oG_{Zr,Vac}^\phi - H_{Zr}^{SER}$ is the temperature dependent molar Gibbs energy of Zr.

The third term on the right hand side of Eq.(3-2), ${}^{id}G_m^\phi$, is the molar Gibbs energy of the ideal mixing of oxygen atoms and vacancies on the interstitial sublattice and is given by,

$${}^{id}G_m^\phi = qRT \left(y_O \ln(y_O) + y_{Vac} \ln(y_{Vac}) \right). \quad (3-5)$$

In Eq. (3-5), R is the ideal gas constant in J mol⁻¹ K⁻¹ and T is the absolute temperature in K. The ideal mixing term represents the contribution to the total Gibbs energy of mixing owed to the entropic contribution by each component.

The final term on the right hand side of Eq.(3-2), ${}^{ex}G_m^\phi$, is the molar Gibbs energy of the excess mixing of oxygen atoms and vacancies on the interstitial sublattice and is given by,

$${}^{ex}G_m^\phi = y_O y_{Vac} \sum_{v=0}^n {}^vL_{Zr,Vac,O}^\phi (y_O - y_{Vac})^v. \quad (3-6)$$

In Eq. (3-6), ${}^vL_{Zr,Vac,O}^\phi$ are temperature dependent ($A+BT$) interaction parameters for the oxygen-vacancy interaction in the interstitial sublattice. The interaction parameters are coefficients for the Redlich-Kister polynomial (the entire right-hand side of Eq. (3-6)) that is usually truncated to $n = 0$ or $n = 1$. Please note that when the first term on the right hand side of Eq. (3-2) ($1 / (1 + qy_O)$) is multiplied by Eqs. (3-5) and (3-6), the mole fraction of oxygen atoms occupying the interstitial sites of the lattice can be described and is given by,

$$x_O = \frac{qy_O}{1 + qy_O}. \quad (3-7)$$

The controversial aspect of Liang *et al.* assessment is found for α Zr at high oxygen solubility (0.15-0.28 atom fraction O) and low temperature (300-770°C). In this region, ordered phases of the hcp lattice, or super-lattices, exist (Liang *et al.* 2001). In these super-lattices, oxygen layers are stacked into definitive sequences in which the oxygen atoms have specific sites in which they occupy within the interstices of the hcp lattice (Liang *et al.* 2001). Liang *et al.* (2001) included the use of a four-sublattice model to describe the order-disorder relationships of α Zr. Since these phases were considered meta-stable by Ondik and McMurdie (1998) in their experimental review of the Zr-O system, they were excluded from this calculation. Please note that phases that formed above 1500°C (face-centered cubic (fcc) zirconia (γ ZrO₂) and the liquid Zr-O phase (Liquid)) were not included in this calculation since they were considered unlikely to form at the deposition temperatures of interest (800–1400°C).

3.1.3 Phase Diagram for the YO_{1.5}-ZrO₂ System

The model used for the yttria-zirconia solid solutions (Table 3-3) were those of Du *et al.* (1992), who assessed the YO_{1.5}-ZrO₂ system. Du *et al.* performed an assessment for this system based on the experimental phase diagram data from Stubican 1988, Pascual and Duran (1983), Stubican (1982), and Scott (1975). The experimental phase diagram (Figure 3-3) was the summation of the experimental XRD work of the authors just mentioned and included the most recent examination by Suzuki, who used electronic conductivity measurements to determine the phase boundaries for the zirconia-rich side of this figure (1995).

The assessment implemented a substitutional solid solution model with Redlich-Kister interaction parameters (Du *et al.* 1992). They gave the model formalism

for the Gibbs energy of ZrO_2 and $\text{YO}_{1.5}$ in the solid solution (G_m) relative to the stable reference enthalpy (H^{SER}) of pure $\text{YO}_{1.5}$ and ZrO_2 at 298 K, as

$$G_m - H^{SER} = {}^{me}G_m + {}^{id}G_m + {}^{ex}G_m. \quad (3-8)$$

In Eq. (3-8), H^{SER} for $\text{YO}_{1.5}$ and ZrO_2 is equal to the heat of formation at 298 K for $\text{YO}_{1.5}$ and ZrO_2 . The first term on the right-hand side of Eq. (3-8) (${}^{me}G_m$) is the mechanical mixing term, which is described by the compositional addition of the pure component molar Gibbs free energy as

$${}^{me}G_m = x_{\text{ZrO}_2} \left(G_{\text{ZrO}_2} - H_{\text{Zr}}^{SER} - 2H_{\text{O}}^{SER} \right) + x_{\text{YO}_{1.5}} \left(G_{\text{YO}_{1.5}} - H_{\text{Y}}^{SER} - 1.5H_{\text{O}}^{SER} \right). \quad (3-9)$$

In Eq. (3-9), H_{Zr}^{SER} , H_{Y}^{SER} , and H_{O}^{SER} are the stable element reference enthalpies at 298 K for zirconium, yttrium, and oxygen, respectively; $x_{\text{YO}_{1.5}}$ and x_{ZrO_2} are the mole fractions of $\text{YO}_{1.5}$ and ZrO_2 , respectively. $G_{\text{ZrO}_2} - H_{\text{Zr}}^{SER} - 2H_{\text{O}}^{SER}$ and $G_{\text{YO}_{1.5}} - H_{\text{Y}}^{SER} - 1.5H_{\text{O}}^{SER}$ are the temperature dependent Gibbs energies for ZrO_2 and $\text{YO}_{1.5}$, respectively.

The second term on the right-hand side of Eq. (3-8) (${}^{id}G_m$) is the ideal mixing term, which is described by the entropic contribution of the mixture as

$${}^{id}G_m = RT \left[x_{\text{ZrO}_2} \ln(x_{\text{ZrO}_2}) + x_{\text{YO}_{1.5}} \ln(x_{\text{YO}_{1.5}}) \right], \quad (3-10)$$

where R is the universal gas constant and T is the absolute temperature.

The third term on the right-hand side of Eq. (3-8) (${}^{ex}G_m$) is the excess Gibbs energy of mixing term, which is represented by a truncated version of the Redlich-Kister polynomial:

$${}^{ex}G_m = x_{\text{ZrO}_2} x_{\text{YO}_{1.5}} \left[{}^0L(T) + {}^1L(T) \left(x_{\text{ZrO}_2} - x_{\text{YO}_{1.5}} \right) \right]. \quad (3-11)$$

The terms ${}^0L(T)$ and ${}^1L(T)$ are parameters that describe the interaction behavior between $\text{YO}_{1.5}$ and ZrO_2 (Smith and Van Ness 1987).

When comparing the experimental results of Suzuki (1995), Stubican (1988), Pascual and Duran (1983), Stubican (1982), and Scott (1975) (Figure 3-3) with the assessed results of Du *et al.* (Figure 3-4), there were noticeable similarities and differences. The calculations of Du *et al.* (1992) not only predicted the solid solutions reasonably well, they also predicted the following reactions:



Similar to Stubican (1982), Du *et al.* (1992) predicted the congruent transformation of $Zr_3Y_4O_{12}$ into *Css* at 1382°C and reconfirmed the peritectic reaction,



However, Du *et al.* (1992) introduced a new eutectoid reaction,



This was not observed experimentally.

In addition, many of the invariant transition temperatures calculated by Du *et al.* (1992) () were higher than those of the experimental results. For example, the invariant transition temperature that serves as the lower bound for the *Tss*+*Mss* and *Tss*+*Css* two-phase regions and as the upper bound for the *Mss*+*Css* region was determined experimentally to occur at 600°C (Figure 3-3), whereas Du *et al.* (1992) calculated this invariant transition temperature to occur at 751°C (Figure 3-4). Despite these differences, Du *et al.* (1992) calculated a reasonable representation of the experimental phase diagram (especially on the zirconia-rich regions) and this phase diagram was used in this study.

3.2 Chemical Vapor Deposition Equilibrium Calculation

Two separate calculations were performed in this calculation. One system included the $\text{YO}_{1.5}\text{-ZrO}_2$ phase diagram information for the Zr-Y-Cl-O-C-H-Inert system and the other calculation used the Zr-O phase diagram information for the Zr-Cl-O-C-H-Inert system.

Several assumptions were used in this calculation. First, the gas phase was considered ideal. Second, the solid solutions were assumed to deposit as separate phases except for the solid solution phases of yttria and zirconia. Finally, the conditions used for calculation were stoichiometric atomic ratios used to generalize the results.

3.2.1 The Zr-Cl-O-C-H-Inert System

Following the restriction given in above, ZrCl_4 and CO_2 were introduced as the stoichiometric restrictions $n_{\text{Cl}} - 4n_{\text{Zr}} = 0$ and $2n_{\text{C}} - n_{\text{O}} = 0$, respectively. The basis of the calculation was taken to be $n_{\text{O}} + n_{\text{Zr}} = 0.001$. With that in mind, five degrees of freedom must be specified to satisfy the Gibbs phase rule to perform a calculation. Thus, temperature, pressure, and the following atomic ratios will be used:

$$n_{\text{O}} / n_{\text{Zr}} \quad (3-16)$$

$$n_{\text{H}} / n_{\text{C}} \quad (3-17)$$

$$n_{\text{Inert}} / (n_{\text{Zr}} + n_{\text{O}} + n_{\text{H}} + n_{\text{Cl}} + n_{\text{C}}) \quad (3-18)$$

Variable (3-16) was interchanged with the ratio $n_{\text{O}} / (n_{\text{O}} + n_{\text{Zr}})$ by,

$$n_{\text{O}} / (n_{\text{O}} + n_{\text{Zr}}) = 1 - \left(\frac{n_{\text{O}}}{n_{\text{Zr}}} + 1 \right)^{-1}, \quad (3-19)$$

where $n_{\text{O}} / (n_{\text{O}} + n_{\text{Zr}})$ is the composition of oxygen in metallic Zr for both the αZr βZr phases. Variable (3-17) was interchanged with,

$$n_H / (n_{Zr} + n_O + n_{Inert} + n_{Cl} + n_C) \quad (3-20)$$

to study the effect of using hydrogen carrier gas. Variable (3-18) has the same effect as Variable (3-24), and thus was fixed for each calculation.

Illustrated in Figure 3-5 is the calculated effect of the inlet n_O / n_{Zr} ratio and temperature on phase formation. Single-phase formation of tetragonal zirconia (βZrO_2) occurred at all n_O / n_{Zr} ratios and a typical deposition temperature of 1250°C. Moreover, efficient ZrCl_4 precursor utilization occurred for n_O / n_{Zr} ratios greater than 4 (Figure 3-6) to form βZrO_2 at 1250°C. Further, this efficient deposition of βZrO_2 was reflected in Figure 3-7, where all of the available Zr atoms were incorporated as βZrO_2 .

Conversely, single-phase deposition of monoclinic zirconia (αZrO_2) occurred at lower temperatures (< 1205°C), Figure 3-5). Single phase formation of αZrO_2 , however, did not influence deposition efficiency, where all of the available Zr atoms were incorporated as αZrO_2 for n_O / n_{Zr} ratios greater than 4. Since αZrO_2 and βZrO_2 were treated as line compounds in the calculation, these phases were stoichiometric with a desirable coating composition $((n_O / n_{Zr})_{\text{coating}} = 2 \text{ or } (n_O / (n_O + n_{Zr}))_{\text{coating}} = 0.67)$. ..

In contrast to the results above, secondary phase formation of carbon occurred with increasing n_H / n_C ratios. This secondary phase formation is illustrated in Figure 3-8, which shows the effect of increasing the n_H / n_C ratio as it relates to increasing n_O / n_{Zr} ratios and temperature. Figure 3-8 is very similar to Figure 3-5 except the n_H / n_C ratio was allowed to be fixed at values of 3, 5, 7, and 10. The line at 1205°C is the phase boundary between αZrO_2 and βZrO_2 , which did not vary with the n_H / n_C ratio. The various dashed and dot-dashed lines are boundaries of fixed n_H / n_C below which carbon formation is superimposed on the equilibrium phase formation of zirconia.

This formation of carbon is undesirable, so it is useful to understand the reason for its occurrence. The results shown in Figure 3-8 are reflected in Figure 3-9 which describes the gas phase equilibria as a function of the increasing n_H / n_C ratio (from 1 to 10) at 1000°C and an inlet n_O / n_{Zr} ratio of 1. As n_H / n_C increased, the CO and CO₂ content decreased and the H₂ content increased. The carbon formation is attributed to the high activity of carbon due to the [CO]/[CO₂] ratio being greater than unity at equilibrium for n_H / n_C ratios greater than unity.

Similarly, decreasing the pressure reduced the likeliness of carbon deposition (Figure 3-10). For example, the carbon boundary lines decreased in temperature (from 1065°C to 910°C) as pressure was reduced (from 10⁵ Pa to 10³ Pa). The carbon boundary shifted toward lower temperatures as the pressure decreases (LeChatelier's principle).

ZrC formation was also possible. In Figure 3-10, it can be seen that at 1 kPa, formation of ZrC occurred at high temperatures and low n_O / n_{Zr} ratios. This result is coupled with the high hydrogen content ($n_H / n_C = 10$) in the system and will be discussed in more detail in later sections.

The efficiency of carbon deposition was important as it showed the relative amount of carbon formed. As much as 22% ($100\% \times n_{C, graph} / n_{C, inlet}$) of the inlet carbon accumulated as graphite at low oxygen content ($n_O / n_{Zr} = 1$), relatively high pressure (10⁵ Pa), and moderate temperatures (800°C) (Figure 3-11). This maximum efficiency was reduced markedly by reducing the inlet hydrogen content (n_H / n_C), reducing pressure, and increasing the deposition temperature. These trends concur with the result obtained in Figure 3-22 for the Zr-Y-Cl-O-C-H-Inert system.

If the inert carrier gas is replaced with hydrogen, single-phase formation of zirconia becomes more difficult (n_O / n_{Zr} ratios < 4 , Figure 3-12). The use of hydrogen carrier gas caused the formation of alternative Zr phases (α Zr and β Zr) with low coating oxygen content. For example, at 11000°C and n_O / n_{Zr} ratio of 4×10^{-4} , β Zr is predicted to form with a coating composition of $(n_O / n_{Zr})_{\text{coating}} = 0.02 ((n_O / (n_O + n_{Zr}))_{\text{coating}} = 0.0196)$. The fact that these phases formed at such low inlet n_O / n_{Zr} ratios indicated that there was insufficient system oxygen. This resulted in excess Zr atoms that combined with carbon atoms and formed ZrC. Despite these findings, single-phase formation of β ZrO₂ still occurred at temperatures above 1205°C (Figure 3-12) with complete ZrCl₄ utilization for n_O / n_{Zr} ratio in excess of 4 (Figure 3-13)

3.2.2 The Zr-Y-Cl-O-C-H-Inert System

Thermochemical equilibrium diagrams were computed in this work using the ThermoCalc computational software package (Sundman 1985). The inlet variables were expressed in atomic ratios to generalize the results. The variables explored were the atomic ratios:

$$n_O / (n_Y + n_{Zr}), \quad (3-21)$$

$$n_Y / (n_Y + n_{Zr}), \quad (3-22)$$

$$n_H / n_C, \quad (3-23)$$

$$n_{\text{inert}} / (n_Y + n_{Zr} + n_O + n_H + n_{Cl} + n_C). \quad (3-24)$$

Variable (3-24) represents dilution of the system with inert gas, which indirectly adjusts the species partial pressures. Besides temperature and pressure, three other CVD

conditions were fixed by input moles (n) of the metals ($n_Y + n_{Zr} = 0.001$) and the reagent stoichiometry of input CO_2 ($2n_C - n_O = 0$), and ZrCl_4 , and YCl_3 ($n_{Cl} - 4n_{Zr} - 3n_Y = 0$).

Illustrated in Figure 3-14 is the effect of the inlet $n_O / (n_Y + n_{Zr})$ ratio and temperature on phase formation. For example, a minimum inlet $n_O / (n_Y + n_{Zr})$ ratio of 8 ensured tetragonal YSZ (Tss) formation at a typical deposition temperature of 1000°C. This was reflected in the low equilibrium mole fraction of ZrCl_4 and YCl_3 at high inlet $n_O / (n_Y + n_{Zr})$ ratios, indicating efficient precursor oxidation (Figure 3-15).

In contrast, lower inlet $n_O / (n_Y + n_{Zr})$ ratios yielded the monoclinic (Mss) phase or two-phase mixture of $\text{YCl}_3(s)$ and Mss YSZ (Figure 3-14). This differential in oxidation behavior was seen in Figure 3-16, which illustrated the effect of increasing inlet $n_O / (n_Y + n_{Zr})$ on the incorporation of zirconium and yttrium to form Mss or Tss phases. A negligible amount ($< 10^{-6} \%$) of yttrium was present in the Mss phase up to an inlet $n_O / (n_Y + n_{Zr}) = 6.8$. As the inlet $n_O / (n_Y + n_{Zr})$ ratio was increased to 8, nearly complete incorporation of both yttrium and zirconium was seen, and tetragonal YSZ formed (Figure 3-14 and Figure 3-16). Further, Figure 3-17 reflected this effect of inlet $n_O / (n_Y + n_{Zr})$ ratios on deposit compositions. For example, when the inlet $n_O / (n_Y + n_{Zr})$ ratio was equal to 8 and the inlet $n_Y / (n_Y + n_{Zr})$ ratio was equal to 0.08, the equilibrium deposit was tetragonal YSZ with a $n_Y / (n_Y + n_{Zr})$ ratio of 0.08. If the inlet $n_O / (n_Y + n_{Zr})$ ratio was equal to 6, the inlet $n_Y / (n_Y + n_{Zr})$ ratio must be 0.22 to obtain tetragonal YSZ with a $n_Y / (n_Y + n_{Zr})$ ratio of 0.08. In practical terms, not having a direct correspondence between the inlet atomic ratios and those of the deposit made compositional control difficult and caused inefficient metal source utilization.

In Figure 3-18, the $n_O / (n_Y + n_Z)$ ratio was fixed at 8, while the inlet $n_Y / (n_Y + n_Z)$ ratio and temperature were varied, with the same result calculated for $n_O / (n_Y + n_Z) > 8$. It was seen here that the desired Tss region was favored over significant temperature and inlet $n_Y / (n_Y + n_Z)$ ratio regions. Thus, a large “window” exists to deposit tetragonal YSZ

Co-deposition of carbon with YSZ is typically undesirable. Illustrated in Figure 3-19 was the effect of the inlet n_H / n_C ratio on carbon deposition as it related to temperature and inlet $n_Y / (n_Y + n_Z)$ ratio. The dashed lines are boundaries of fixed inlet n_H / n_C ratio below which carbon forms, and are superimposed on the equilibrium oxide phase regions (solid lines). The results of Figure 3-19 were reflected in Figure 3-20, which described the gas phase equilibria as a function of inlet n_H / n_C ratio at 500°C and an inlet $n_Y / (n_Y + n_Z)$ ratio of 0.08. As the inlet n_H / n_C ratio was increased, the CO and CO₂ mole fractions decreased while the H₂O mole fraction leveled. This result was due to inlet hydrogen consuming the oxygen to form water, thus reducing CO and CO₂ to carbon. Also, note that in Figure 3-20 the [CO]/[CO₂] ratio was greater than unity for inlet n_H / n_C ratios greater than 2, thus the carbon activity increased at inlet n_H / n_C ratios greater than 2 at 500°C.

The effect of overall pressure on carbon deposition was seen in Figure 3-21 over the range 10^3 to 10^5 Pa as a function of temperature and the inlet $n_Y / (n_Y + n_Z)$ ratio. Carbon formed at temperatures below the boundaries (dashed lines). As the pressure was decreased, the carbon formation boundary shifted to lower temperatures (LeChatelier’s principle).

Illustrated in Figure 3-22 are the moles of carbon that deposit at equilibrium relative to the moles of carbon inlet to the system. The amount of carbon deposition was studied as a function of temperature at various pressures and inlet n_H / n_C ratios.

Reflecting earlier results, carbon deposition decreased as (1) temperature increased, (2) the inlet n_H / n_C ratio decreased, and (3) the pressure decreased.

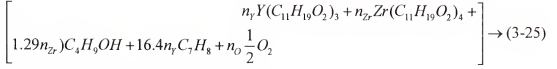
The inlet $n_{Inert} / (n_Y + n_{Zr} + n_O + n_H + n_{Cl} + n_C)$ ratio diluted the gas phase, but had no effect on the deposition of tetragonal YSZ (Figure 3-23).

3.2.3 The Zr-Y-O-C-H System

This calculation was more complex than the calculations thus presented due to the complex stoichiometry of the precursors and their respective solvents. To help identify the CVD variables, it was necessary to analyze the reagent stoichiometry in this system. The stoichiometric degrees of freedom are analyzed first for the $Y(OBu^t)_3$ and $Zr(OBu^t)_4$ precursors and then for the $Y(tmhd)_3$ and $Zr(tmhd)_4$ precursors. Also included in the stoichiometric analysis was the solvents used for each precursors. The following information was needed for the calculation: (1) the solubility of the metal-organic precursors in their respective solvents, (2) the density of the precursor solution or solvent, and, if necessary, (3) the weight percentage of the precursors in their respective solvents. All of the above information helped to evaluate the moles of solvent added to the system based on the moles of each precursor.

The $Y(OBu^t)_3$ and $Zr(OBu^t)_4$ precursors were provided by Aldrich Chemicals, Inc. The solutions were 2.23 M Zr in *n*-butanol and 0.5 M Y in toluene, 0.9 g cm⁻³ in density for the Zr solution and 0.89 g cm⁻³ in density for the Y solution, and 80 wt.%

$Zr(OBut^n)_4$ in *n*-butanol and 17.2 wt% $Y(OBut^n)_3$ in toluene. The reagent-side of the reaction, including these stoichiometric inputs, is



In Eq. (3-25), n_O represents the initial moles of atomic oxygen added to the system.

The first atomic ratio to be considered is $n_Y / (n_Y + n_{Zr})$ and this will be one of the variables in this calculation. This ratio forces the stoichiometry, and thus the entire calculation, to be based on the moles of yttrium and zirconium ($n_Y + n_{Zr}$) input to the reacting system. This basis ($n_Y + n_{Zr}$) will be arbitrarily fixed to 0.001. Thus, $n_Y / (n_Y + n_{Zr})$ varied between 0 and 1 since the moles of yttrium (n_Y) added to the system did not exceed 0.001.

According to Eq. (3-25), the moles of carbon and hydrogen inlet to the system are restricted to the moles of Y and Zr inlet to the system. These relations are given as,

$$n_H - 48.9n_{Zr} - 158.2n_Y = 0, \quad (3-26)$$

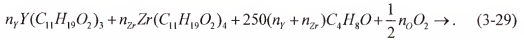
$$n_C - 21.2n_{Zr} - 126.8n_Y = 0 \quad (3-27)$$

Further, since oxygen is present in the precursor solution, the amount of oxygen inlet to the system had a minimum value given by,

$$n_{O,min} - 5.3n_{Zr} - 3n_Y = 0. \quad (3-28)$$

Since molecular oxygen was used for reagent transport and reaction, the amount of oxygen will exceed this minimum value. Thus, another variable, $n_O / (n_Y + n_{Zr})$, was used in this calculation. Since the pressure remained fixed throughout the calculation, the only condition left to be optimized was the temperature.

Following the rationale above, similar restrictions and conditions were used for the calculation involving Y- and Zr- β -diketonate precursors with a tetrahydrofuran (THF) solvent. This calculation used an Y- and Zr- β -diketonate solubility of 0.0085 M and 0.042 M, respectively, in THF based on initial solubility testing (results not shown). Taking the Y and Zr solubility in the precursor solution and the solvent's density (0.888 g cm⁻³), the reagent side of the reaction is:



Thus, the restrictions are:

$$n_H - 2076n_{Zr} - 2057n_Y = 0, \quad (3-30)$$

$$n_C - 1044n_{Zr} - 1033n_Y = 0 \quad (3-31)$$

Further, oxygen was also present in the precursor solution, thus the minimum amount of oxygen added to the system was given by,

$$n_{O,\min} - 258n_{Zr} - 256n_Y = 0. \quad (3-32)$$

Thus, the variables to be optimized with this set of precursors were the $n_O / (n_Y + n_{Zr})$ ratio (above this minimum in Eq. (3-32)), the $n_Y / (n_Y + n_{Zr})$ ratio, and the substrate temperature. The basis, $n_Y + n_{Zr}$, was fixed to 0.001. Finally, the pressure (10³ Pa) remained fixed in this calculation. The calculations were performed for the *n*-butoxide precursors and then followed by the β -diketonate precursors.

Illustrated in Figure 3-24 is the calculated effect of the substrate temperature and the $n_O / (n_Y + n_{Zr})$ ratio on solid phase formation for the *n*-butoxide precursors. On the horizontal axis was increasing oxygen content, where $n_O / (n_Y + n_{Zr}) = 5$ represented the amount of oxygen added to the system by the precursor solution. Any additional oxygen

was added to the system by O_2 . It can be seen that tetragonal YSZ can be formed at high $n_O / (n_Y + n_{Zr})$ ratios (> 30) and high temperatures ($> 950^\circ\text{C}$).

Secondary-phase formation was also observed. It was observed that carbon formation occurred at all temperatures for $n_O / (n_Y + n_{Zr}) < 30$ (Figure 3-24). This low oxygen content increases the carbon activity, which was evident by the large $[\text{CO}]:[\text{CO}_2]$ ratio at equilibrium (Figure 3-26), which increases the likeliness of carbon formation (as presented earlier).

At even lower oxygen content ($n_O / (n_Y + n_{Zr}) < 10$) and high temperature ($T > 1050^\circ\text{C}$) (Figure 3-25), ZrC formation was predicted. ZrC formation occurred with more yttria-rich deposition of YSZ (i.e. C_{ss} YSZ), due to the lack of full Zr incorporation in the metal oxide deposit. Although full Zr incorporation was not seen (Figure 3-27), full yttrium incorporation was seen in C_{ss} YSZ (Figure 3-28). This means that the low system oxygen was insufficient to oxidize Zr fully to form T_{ss} YSZ. Moreover, the low system oxygen was insufficient to oxidize C fully. This means that unutilized Zr and C atoms reacted to form ZrC.

The presence of each element in the gas or condensed phases (Figure 3-27 to Figure 3-30) are insightful for efficiency studies. In Figure 3-29, carbon was seen to be invariant (remains in the gas phase as either CO or CO₂) for high $n_O / (n_Y + n_{Zr})$ ratios (> 30). This means that the formation of carbon is inefficient, which is desirable since this minimizes or eliminates possible coating contamination.

Similarly, oxygen was seen to have a large gas phase presence for all $n_O / (n_Y + n_{Zr})$ ratios (Figure 3-30), yet, several interesting observations were seen. First, the T_{ss} oxygen content rose while the C_{ss} oxygen content decreased ($n_O / (n_Y + n_{Zr}) < 10$,

Figure 3-30). This was due to the C_{ss} phase becoming less stable and the T_{ss} phase becoming more stable with increasing system oxygen (as presented above). Second, Figure 3-30 showed a “dip” in the oxygen content ($n_O / (n_Y + n_{Zr})$ ratio of 10). This was due to the increased incorporation of zirconium in the metal oxide deposit to form the T_{ss} phase. Finally, when the $n_O / (n_Y + n_{Zr})$ ratio was increased above 10, the oxygen content was predominantly in the gas phase. This means that the oxygen content does not decrease in the T_{ss} phase, just that the T_{ss} phase is fully oxidized and any additional oxygen remains in the gas phase.

Figure 3-31 showed the effect of varying the inlet $n_Y / (n_Y + n_{Zr})$ ratio and temperature on solid phase formation. It was seen that carbon-free tetragonal YSZ was obtained provided the $n_Y / (n_Y + n_{Zr})$ ratio remained at 0.08 and the temperature remained above 950°C. When the $n_Y / (n_Y + n_{Zr})$ ratio exceeded 0.45, however, carbon was predicted to form. This increased carbon activity was evident by the high $[CO]:[CO_2]$ ratio in the gas phase at equilibrium ($n_Y / (n_Y + n_{Zr}) > 0.45$, Figure 3-32).

Figure 3-33 illustrated the calculated effect of the substrate temperature and the $n_O / (n_Y + n_{Zr})$ ratio on solid phase formation for the β -diketonate precursors. On the horizontal axis was increasing oxygen content, where $n_O / (n_Y + n_{Zr}) = 250$ represented the amount of oxygen added to the system by the precursor solution. Any additional oxygen was added to the system by O_2 . It was seen that tetragonal YSZ was formed at high $n_O / (n_Y + n_{Zr})$ ratios (> 1050) and high temperatures ($> 950^\circ\text{C}$).

Secondary phase formation of carbon was also observed. The reason for carbon formation was illustrated in Figure 3-34. As presented earlier, the formation of carbon was owed to the increased carbon activity. This increased carbon activity was evident by

the high $[\text{CO}]:[\text{CO}_2]$ ratio at equilibrium in the gas phase ($n_{\text{O}} / (n_{\text{Y}} + n_{\text{Zr}}) < 1050$, Figure 3-34).

Finally, it should be noted that ZrC formation was inhibited while using the β -diketonate precursors. This was simply due to the high oxygen presence in the precursor solution. In addition, yttrium, zirconium, and oxygen atoms were fully incorporated in the Tss YSZ films. Thus, the utilization of both yttrium and zirconium was very nearly 100%. Thus, it was unnecessary to study the efficiency of deposition.

3.3 Discussion

For purposes of comparison, Table 2.1 and Table 2.2 summarize the experimental results of previous authors in depositing zirconia, yttria, and YSZ using chloride precursors.

For chloride CVD, excess oxygen (relative to the inlet metal content) and high temperature are generally found necessary to obtain carbon-free, pure tetragonal zirconia and yttria-stabilized tetragonal zirconia. Similarly, in their equilibrium analysis of the deposition of zirconia, Minet *et al.* (1986) found that $n_{\text{O}} / n_{\text{Zr}}$ ratios greater than 4 ($[\text{CO}_2]_{\text{inlet}} / [\text{ZrCl}_4]_{\text{inlet}} \geq 2$), which fulfills the stoichiometric necessity to fully oxidize ZrCl_4 , were needed to efficiently deposit the monoclinic or tetragonal phase of pure zirconia. This result was later confirmed experimentally by Minet *et al.* (1987) and Sipp *et al.* (1992a), who found that high $n_{\text{O}} / n_{\text{Zr}}$ ratios (≥ 17) were needed to efficiently deposit ZrO_2 from ZrCl_4 (Figure 3-18 and Table 2.1).

Confirming the greater difficulty in oxidizing the yttrium precursor, Sipp *et al.* (1992b) experimentally observed that the $n_{\text{O}} / n_{\text{Y}}$ ratio needed to be at least 18 ($[\text{CO}_2]_{\text{inlet}} / [\text{YCl}_3]_{\text{inlet}} \geq 9$) and the temperature had to be at least 1100°C to ensure pure yttria

deposition (Figure 3-18 and Table 2.1). They suggested that such a high oxygen requirement was due to the formation of condensed phase yttrium oxy-chloride (YOCl). This condensed phase was not considered in the calculations reported here because no reliable source of its thermochemical properties was found and was not needed to demonstrate the relatively high oxygen potential required for $\text{YCl}_{3(g)}$ oxidation. Condensed phase YCl_3 , however, did form, suggesting that ineffective deposition conditions could lead to coatings with insufficient yttrium incorporation. Wahl *et al.* (1979), who performed experimental YSZ deposition, also observed that a high $n_{\text{O}} / (n_{\text{Y}} + n_{\text{Zr}})$ of 16 is required to fully oxidize YCl_3 and ZrCl_4 to the cubic phase of YSZ (Figure 3-18). In this case, the $n_{\text{Y}} / (n_{\text{Y}} + n_{\text{Zr}})$ ratio was 0.22, which further emphasizes the impact that yttrium addition has on the oxygen requirement to efficiently produce YSZ. Further, Wahl *et al.* (1979) obtained cubic YSZ at approximately 10 mol% Y_2O_3 (or a film $n_{\text{Y}} / (n_{\text{Y}} + n_{\text{Zr}}) = 0.18$) by using an inlet $n_{\text{Y}} / (n_{\text{Y}} + n_{\text{Zr}})$ ratio of approximately 0.22. This means that precursor utilization is approximately 81%, which is very close to the value of 100% predicted in this work. This result matches very closely the results of Yamane and Harai (1989), in which they used a much higher $n_{\text{O}} / (n_{\text{Y}} + n_{\text{Zr}})$ ratio. Thus, the observation in this work that an inlet $n_{\text{O}} / (n_{\text{Y}} + n_{\text{Zr}}) > 8$ is needed to form YSZ agrees well with the values determined by others when the proportion of yttrium with zirconium is considered.

Four variables affected carbon formation: the inlet $n_{\text{H}} / n_{\text{C}}$ ratio, temperature, total pressure, and the inlet $n_{\text{Y}} / (n_{\text{Y}} + n_{\text{Zr}})$ ratio. The inlet $n_{\text{H}} / n_{\text{C}}$ ratio, which had the largest impact, when increased favored carbon formation at higher temperatures. Excess hydrogen reduces CO_2 to form H_2O and CO via the RWGSR. Minet *et al.* (1987)

suggested carbon deposits because of the further reduction of CO to form carbon and more water vapor. This is seen in Figure 3-20, where a decrease in the CO partial pressure and an increase in the H₂O partial pressure coincide with a rise in the inlet hydrogen content. The same results were seen for pure oxide formation of βZrO_2 . Consequently, the carbon activity increases, promoting solid carbon formation.

Discrepancies exist between this work and others on the influence of pressure on carbon deposition. The experimental work on the CVD of zirconia by Minet *et al.* shows that the likelihood of carbon deposition decreased as pressure increased (1987). In their equilibrium analysis, however, Minet *et al.* (1986) found that carbon deposition did not depend on pressure. According to LeChatelier's principle, though, increased pressures resulted in an equilibrium shift such that carbon formation was more likely. The equilibrium calculations of Minet *et al.* (1986) and experimental results of Minet *et al.* (1987) contradicted each other and the results reported here and by Lhermitte-Sebire *et al.* (1986)

A consequence of high system hydrogen content was the formation of ZrC (and possibly αZr). This was predicted for deposition at high temperatures and low system oxygen ($n_{\text{O}}/n_{\text{Zr}} < 4$, Figure 3-12). ZrC formed not only because the system had a low overall oxygen content, but also because of the excess hydrogen relative to carbon ($n_{\text{H}}/n_{\text{C}}$) (Ducarrior *et al.* (1985, Reynolds 1974, Ikawa 1972, Ikawa and Iwamoto 1972, Reynolds and Kaae 1975, Naito *et al.* 1978, Davies *et al.* 1963). If hydrogen was not added in excess of this value relative to carbon, however, the result obtained in Figure 3-5 occurred.

Furthermore, reduced pressure increased the likeliness of ZrC formation. This of course cannot occur without excess hydrogen (as discussed above). According to LeChatelier's principle, a decreased pressure shifted this reaction towards the formation of ZrC.

For MOCVD, excess oxygen was required to ensure pure oxide formation of tetragonal YSZ. This means that the amount of oxygen inherent in the precursor solutions ($n_O / (n_Y + n_{Zr}) = 5$ in Figure 3-24 and $n_O / (n_Y + n_{Zr}) = 250$ in Figure 3-33) is insufficient for pure metal oxide formation.

The need for the additional oxygen was due to the addition of the solvent. The β -diketonate precursors had a comparatively low solubility in THF (Eq. (3-29)). The low solubility of the β -diketonate precursors led to significant levels of carbon in the system. This high carbon content required very high oxygen content ($n_O / (n_Y + n_{Zr}) > 1050$) to maintain carbon in the gas phase as CO or CO₂ (Figure 3-34) and prevent solid carbon formation (Figure 3-33). In the equilibrium analysis by Fredricksson *et al.* (1996), they obtained pure zirconia formation from Zr(tmhd)₄ and O₂ when the n_O / n_{Zr} ratio was 161.6 ($\omega > 0.8$, Table 2.2). The oxygen requirement in this work exceeded that of Fredricksson *et al.* (1996), thus, "bringing to light" the effect of solvent addition.

Conversely, comparatively low oxygen content ($n_O / (n_Y + n_{Zr}) > 30$) was required for pure metal oxide formation using the *n*-butoxide precursors (Figure 3-24). This was due to the high solubility of Zr(OButⁿ)₄ in *n*-butanol and the low yttrium requirement for tetragonal YSZ formation (Eq. (3-25)).

This oxygen requirement became insufficient, however, when yttria-rich phases (Y_{ss} and $\text{Zr}_3\text{Y}_4\text{O}_{12}$) of YSZ were formed (Figure 3-31). This was due to the comparatively moderate solubility of $\text{Y}(\text{OBut}^n)_3$ in toluene as compared to $\text{Zr}(\text{OBut}^n)_4$ in *n*-butanol (Eq. (3-25)). When the yttrium content increased, the carbon content increased significantly. This led to the increased carbon activity ($[\text{CO}]:[\text{CO}_2] > 1$, Figure 3-32) and subsequent solid carbon formation (Figure 3-31).

Deposition using the *n*-butoxide precursors in low system oxygen was deleterious. First, alternative phases of YSZ (C_{ss}) were formed due to the complete utilization of the Y source (Figure 3-28) and incomplete utilization of the Zr source (Figure 3-27). The reason for this preferential utilization is not fully understood, thus, only a partial explanation can be given. The lack of thermochemical information with regard to the $\text{Y}(\text{OBut}^n)_3$ precursor and other species involving yttrium were not found in standard compendia, and thus, were not included. The only available thermochemical information that were pertinent to this calculation were the Y-O species and phases and the pure metal Y phases, thus limiting the species and phases for which Y resided. Since there was enough system oxygen and no available thermochemical species were available for metal-organic species, Y had no other phase to reside except YSZ phases.

The incomplete utilization of the Zr source for YSZ formation was due to its reaction with C to form ZrC. Reflecting the earlier results from chloride CVD, the reaction to form ZrC occurred at low oxygen content, high temperature, and high hydrogen atmospheres. For example, at 1100°C, hydrocarbon species are not stable in sufficient quantities, which is evident by the low content of these hydrocarbon species and high content of H, CO, and H₂ in the gas phase (Figure 3-26). This is similar to the

conditions for ZrC formation in chloride CVD, suggesting the excess hydrogen and high temperature drive the formation of ZrC. This causes more yttria-rich phases of YSZ to form due to diminished incorporation of zirconium at these conditions. The fact that ZrC formation did not occur while using the metal-b-diketonate precursors in the THF solvent suggests that there is enough inherent oxygen in the precursor and in the solvent to preclude formation of ZrC.

In comparing the results of MOCVD and chloride CVD, several similarities and differences were apparent. On one hand, high temperatures and high oxygen content promoted pure metal oxide formation of both zirconia and YSZ without secondary phase formation. Further, precursor utilization was nearly 100%. Finally, ZrC formation was feasible at low system oxygen, high system hydrogen, and high temperature.

On the other hand, more oxygen was required in MOCVD to achieve this pure metal oxide formation. This was due to the high level of carbon associated with the metal-organic precursors and their solvents. Further, condensed phases of Y did not appear in MOCVD whereas condensed phase yttrium tri-chloride did form when the temperature and oxygen content were too low.

Table 3-1. Thermochemical Properties

Species	ΔH_f^{298} kJ mol ⁻¹	S^{298} J mol ⁻¹ K ⁻¹	C_p^a J mol ⁻¹ K ⁻¹	$b \times 10^3$ J mol ⁻¹ K ⁻²	$c \times 10^5$ J mol ⁻¹ K ⁻³	$d \times 10^6$ J mol ⁻¹ K	Range (°C)	Ref.
Y (g)	424.676	179.169	27.552	-8.379	2.786	0.056	T ≤ 5000	Barin (1989)
Y ₂ O (g)	-2.160	283.660	49.144	15.165	-7.240	0.423	T ≤ 5000	Sundman (1985)
			58.084	0.046	-0.005		T ≤ 5000	Sundman (1985)
Y ₂ O ₂ (g)	-556.850	294.200	49.555	60.422	-31.67	-0.511	T ≤ 5000	Sundman (1985)
			82.064	0.523	-0.066	-3.484	T ≤ 5000	Sundman (1985)
YCl ₃ (g)	-702.900	351.500	83.680			-0.523	T ≤ 5000	Kubaschewski <i>et al.</i> (1996)
YO (g)	-45.775	231.780	30.586	11.596	-5.426	-0.186	T ≤ 5000	Sundman (1985)
			40.603	-2.979	0.848	-1.793	T ≤ 5000	Sundman (1985)
YO ₂ (g)	-437.140	265.850	44.874	23.673	-12.04	-0.564	T ≤ 5000	Sundman (1985)
			58.017	0.074	-0.008	-1.822	T ≤ 5000	Sundman (1985)
Zr (g)	610.027	183.027	16.990	8.701	-0.886	0.542	T ≤ 5000	Sundman (1985)
Zr ₂ (g)	904.460	262.350	37.137	0.641	0.026	-0.171	T ≤ 5000	Sundman (1985)
			39.334	2.039	-0.366	-	T ≤ 5000	Sundman (1985)
ZrCl ₂ (g)	186.188	292.571	63.008	-2.347	1.678	-0.428	T ≤ 5000	Barin (1989)
ZrCl ₃ (g)	-524.255	339.013	79.832	10.376	-3.320	-0.598	T ≤ 5000	Barin (1989)
ZrCl ₄ (g)	-869.979	367.716	107.630	0.351	-0.072	0.847	T ≤ 5000	Barin (1989)
ZrCl (g)	205.434	254.497	37.119	0.553	0.043	-0.303	T ≤ 5000	Barin (1989)
ZrH (g)	516.300	217.190	23.042	21.423	-8.814	0.093	T ≤ 5000	Barin (1989)
			37.037	0.762	-0.012	-2.042	T ≤ 5000	Barin (1989)

Table 3-1. Continued

Species	ΔH_f^{298} kJ mol ⁻¹	S^{298} J mol ⁻¹ K ⁻¹	C_p^a J mol ⁻¹ K ⁻¹	$b \times 10^3$ J mol ⁻¹ K ⁻²	$c \times 10^5$ J mol ⁻¹ K ⁻³	$d \times 10^{-6}$ J mol ⁻¹ K ⁻⁴	Range (°C)	Ref.
ZrO (g)	58.576	227.426	11.534	40.565	-	-	T ≤ 5000	Barin (1989)
ZrO ₂ (g)	-286.186	273.751	54.607	2.708	-0.511	-	T ≤ 5000	Barin (1989)
C (graph ^a)	0.000	5.700	0.110	38.940	-	-0.148	T ≤ 5000	Barin (1989)
Y (hcp ^b)	0.000	45.434	24.310	6.814	0.356	0.013	T ≤ 5000	Kubaschewski <i>et al.</i> (1996)
Y (bcc ^c)	4.688	46.683	20.941	-	45.523	0.0109	T ≤ 1479	Dinsdale (1991)
			35.02	15.992			1479	Barin (1989)
YO _{1.5} (hcp)	-	99.068	44.168	23.476			T ≤ 5000	Du <i>et al.</i> (1992)
YO _{1.5} (bcc)	-	82.539	121.930				T ≤ 5000	Du <i>et al.</i> (1992)
YCl ₃ (m ^d)	-999.976	136.817	104.710	3.227	-0.003	-1.211	T ≤ 5000	Kubaschewski <i>et al.</i> (1996)
Zr (hcp)	0.000	38.869	25.198	0.394	5.550	-0.054	T ≤ 5000	Dinsdale (1991), NIST-JANAF (1999)
Zr (bcc)	4.810	43.192	25.607	0.680	0.006	-	T ≤ 1855	Dinsdale (1991), NIST-JANAF (1999)
ZrC (c ^e)	-196.648	33.321	51.287	3.241	0.009	-1.305	T ≤ 5000	Barin (1989)
ZrCl ₂ (r ^f)	-430.952	110.039	73.114	13.842	-0.640	-0.407	T ≤ 5000	Barin (1989)
ZrCl ₃ (h ^g)	-714.209	145.603	99.226	13.515	-0.028	-0.627	T ≤ 5000	Barin (1989)
ZrCl ₄ (c)	-979.809	181.418	124.960	14.167	-0.017	-0.836	T ≤ 5000	Barin (1989)
ZrO ₂ (m)	-	50.347	67.506	9.827		-1.271	T ≤ 2710	Du <i>et al.</i> (1992)
ZrO ₂ (t ^h)	-	40.8	80.300	2.175			T ≤ 2710	Du <i>et al.</i> (1992)

Table 3-1. Continued

Species	ΔH_f^{298}	S^{298}	C_p				Range	Ref.
	kJ mol^{-1}	$\text{J mol}^{-1} \text{K}^{-1}$	$\text{J mol}^{-1} \text{K}^{-1}$	$\text{a} \times 10^3$	$\text{b} \times 10^3$	$\text{c} \times 10^5$	$\text{d} \times 10^{-6}$	
				$\text{J mol}^{-1} \text{K}^{-2}$	$\text{J mol}^{-1} \text{K}^{-3}$	$\text{J mol}^{-1} \text{K}^{-1}$	(°C)	
ZrO ₂ (fcc ⁱ)	- 1101.382	39.085			80.000		T ≤ 2710	Du <i>et al.</i> (1992)

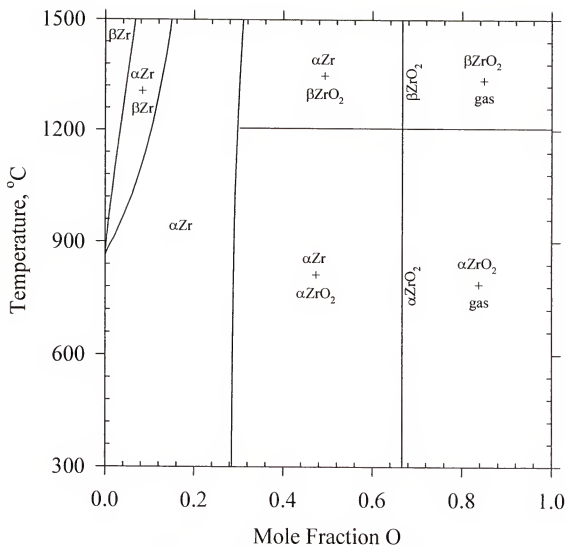
^a graphite (graph), ^b hexagonal close-packed, ^c body-centered cubic (bcc), ^d monoclinic (m), ^e simple cubic (c), ^f rhombohedral (r), ^g hexagonal (h), ^h tetragonal (t), ⁱ face-centered cubic (fcc)

Table 3-2. Interaction Parameters for the Zr-O Assessed Phase Diagram
Source: Liang *et al.* (2001)

Phase	Parameter	Value
βZr	$G_{\text{Zr-O}}^{\text{bcc}} - G_{\text{Zr}}^{\text{bcc}} - 3G_{\text{O}}^{\text{gas}}$	400000.00
	${}^0L_{\text{Zr-O,Vac}}^{\text{bcc}}$	$-2639295.07 + 280.87040T$
	${}^1L_{\text{Zr-O,Vac}}^{\text{bcc}}$	-578130.00
αZr	$G_{\text{Zr-O}}^{\text{hcp}} - G_{\text{Zr}}^{\text{hcp}} - G_{\text{O}}^{\text{gas}}$	$-467447.03 + 79.30340T$
	${}^0L_{\text{Zr-O,Vac}}^{\text{hcp}}$	$-56003.38 + 4.30692T$
	${}^1L_{\text{Zr-O,Vac}}^{\text{hcp}}$	$-3982.58 - 1.94412T$
αZrO_2	$G_{\text{Zr-O}}^{\alpha\text{ZrO}_2} - G_{\text{Zr}}^{\text{hcp}} - 2G_{\text{O}}^{\text{gas}}$	$-1103376.9 + 247.58658T - 8.076129T\ln(T)$
βZrO_2	$G_{\text{Zr-O}}^{\beta\text{ZrO}_2} - G_{\text{Zr}}^{\text{hcp}} - 2G_{\text{O}}^{\text{gas}}$	$-1036480.92 - 267.13659T + 59.015088T\ln(T)$ $- 0.017726352T^2$
gas	$G_{\text{O}}^{\text{gas}} - H_{\text{O}}^{\text{gas}}$	$-3480.87 - 25.503038T - 11.136T\log(T) -$ $0.005098888T^2 + 6.61846(10^{-7})T^3 - 38365T^{-1}$ $25 \leq T \leq 726.85$
	$G_{\text{O}}^{\text{gas}} - H_{\text{O}}^{\text{gas}}$	$-6568.763 + 12.65988T - 16.8138T\log(T) -$ $5.95798(10^{-4})T^2 + 6.781(10^{-9})T^3 + 262905T^{-1}$ $726.85 \leq T \leq 3026.85$
	$G_{\text{O}}^{\text{gas}} - H_{\text{O}}^{\text{gas}}$	$-13986.728 + 31.259625T - 18.9536T\log(T) -$ $4.25243(10^{-4})T^2 + 1.0721(10^{-8})T^3 + 4383200T^{-1}$ $3026.85 \leq T \leq 5000$
	$G_{\text{Zr}}^{\text{bcc}} - G_{\text{Zr}}^{\text{hcp}}$	$7302.056 - 0.70335T - 1.445606T\ln(T) +$ $4.037826(10^{-3})T^2 - 9.7289735(10^{-9})T^3 -$ $7.6142894(10^{-11})T^4 - 9737.0T^{-1}$ $25 \leq T \leq 1854.85$
βZr	$G_{\text{Zr}}^{\text{bcc}} - G_{\text{Zr}}^{\text{hcp}}$	$-4620.034 + 1.55998T + 1.41035E+32T^{-9}$ $1854.85 \leq T \leq 5000$
	$G_{\text{Zr}}^{\text{hcp}} - H_{\text{Zr}}^{\text{hcp}}$	$-7827.595 + 125.64905T - 24.1618T\log(T) -$ $4.37791(10^{-3})T^2 + 34971T^{-1}$ $-143.15 \leq T \leq 1854.85$
	$G_{\text{Zr}}^{\text{hcp}} - H_{\text{Zr}}^{\text{hcp}}$	$-26085.921 + 262.724183T - 42.144T\log(T) -$ $1342.895(10^{28})T^{-9}$ $1854.85 \leq T \leq 5000$
	$G_{\text{Zr}}^{\text{hcp}} - H_{\text{Zr}}^{\text{hcp}}$	

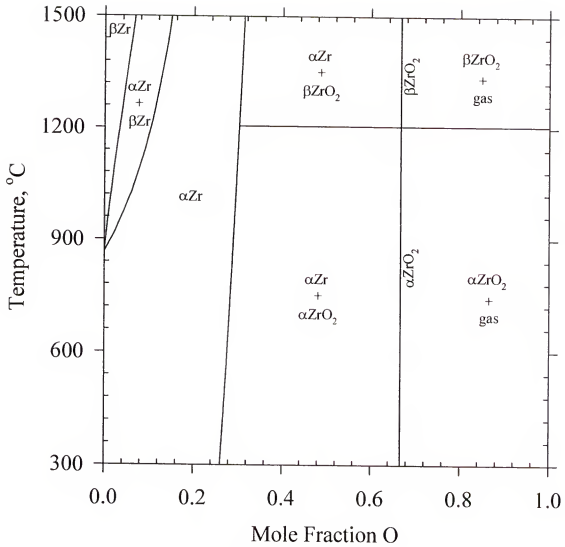
Table 3-3. Optimized lattice stabilities and interactions for the $\text{ZrO}_2\text{-YO}_{1.5}$ system

Phase	Range ($^{\circ}\text{C}$)	Parameter and Value
Monoclinic	25<T<2710	$G_{\text{ZrO}_2}(\text{T/K}) - H_{\text{Zr}}^{\text{SER}} - 2H_{\text{O}}^{\text{SER}}$ -1125386.9 + 411.83491T - 67.5063Tln(T) - 0.00491334T ² + 635630T ⁻¹
	2710<T	$G_{\text{ZrO}_2}(\text{T/K}) - H_{\text{Zr}}^{\text{SER}} - 2H_{\text{O}}^{\text{SER}}$ -1139046.7 + 564.80249T - 87.864Tln(T) - 5.46242E + 33T ⁻⁹
Tetragonal	25<T<2710	$G_{\text{ZrO}_2}(\text{T/K}) - H_{\text{Zr}}^{\text{SER}} - 2H_{\text{O}}^{\text{SER}}$ -1124404.1 + 495.89773T - 80.2998Tln(T) + 0.00108741T ²
	2710<T	-1161302.3 + 571.8733T - 87.864Tln(T) + 8.71E + 33T ⁻⁹
Cubic	25<T<2710	$G_{\text{ZrO}_2}(\text{T/K}) - H_{\text{Zr}}^{\text{SER}} - 2H_{\text{O}}^{\text{SER}}$ -1125234.1 + 496.72262T - 80Tln(T)
	2710<T	$G_{\text{ZrO}_2}(\text{T/K}) - H_{\text{Zr}}^{\text{SER}} - 2H_{\text{O}}^{\text{SER}}$ -1151298.9 + 568.29043T - 87.864Tln(T) + 4.87454E + 33T ⁻⁹
Monoclinic	25<T<2439	$G_{\text{YO}_{1.5}}(\text{T/K}) - H_{\text{Y}}^{\text{SER}} - 1.5H_{\text{O}}^{\text{SER}}$ -908072.6 + 252.50816T - 44.168Tln(T) - 0.01173815T ² + 1.674935E - 21T ⁷
	2439<T	$G_{\text{YO}_{1.5}}(\text{T/K}) - H_{\text{Y}}^{\text{SER}} - 1.5H_{\text{O}}^{\text{SER}}$ -929344 + 511.2415T - 79.84686Tln(T)
Tetragonal	25<T<2439	$G_{\text{YO}_{1.5}}(\text{T/K}) - H_{\text{Y}}^{\text{SER}} - 1.5H_{\text{O}}^{\text{SER}}$ -928992.6 + 249.05556T - 44.168Tln(T) - 0.01173815T ² + 1.674935E - 21T ⁷
	2439<T	$G_{\text{YO}_{1.5}}(\text{T/K}) - H_{\text{Y}}^{\text{SER}} - 1.5H_{\text{O}}^{\text{SER}}$ -950264 + 507.789T - 79.84686Tln(T)
Cubic	25<T<2439	$G_{\text{YO}_{1.5}}(\text{T/K}) - H_{\text{Y}}^{\text{SER}} - 1.5H_{\text{O}}^{\text{SER}}$ -973912.1 + 253.25943T - 44.168Tln(T) - 0.01173815T ²
	2439<T	$G_{\text{YO}_{1.5}}(\text{T/K}) - H_{\text{Y}}^{\text{SER}} - 1.5H_{\text{O}}^{\text{SER}}$ -975905.8 + 504.52886T - 79.84686Tln(T) - 6.693289E + 33T ⁻⁹
$\text{Zr}_3\text{Y}_4\text{O}_{12}$	T < 5000	$(3/7) (G_{\text{ZrO}_2}(\text{T/K}) - H_{\text{Zr}}^{\text{SER}} - 2H_{\text{O}}^{\text{SER}}) + (4/7) G_{\text{YO}_{1.5}}(\text{T/K}) -$ $H_{\text{Y}}^{\text{SER}} - 1.5H_{\text{O}}^{\text{SER}} + 5173.7 + 6.99144\text{T}$
Mss	T < 5000	⁰ L = 74297.0 + 98.12601T
Tss	T < 5000	⁰ L = -44896.8 + 2.95165T
Css/Yss	T < 5000	⁰ L = +12979.8 - 2.86377T ¹ L = -13.50839T



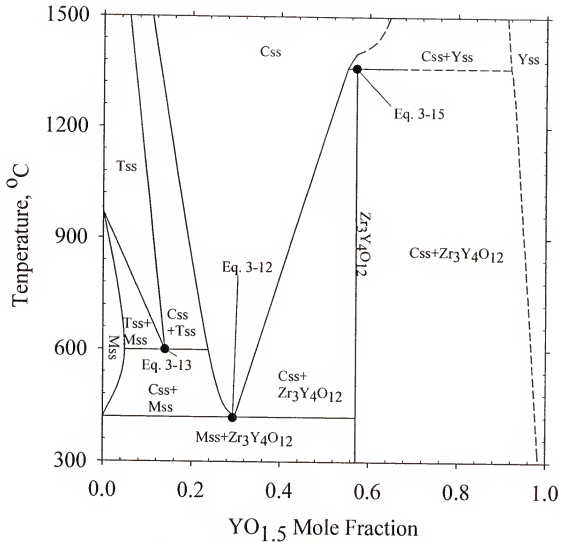
Adapted from: Ondik and McMurdie (1998)

Figure 3-1. Experimental phase diagram of the Zr-O system.
 Ondik, H. M. and H. F. McMurdie., *Phase Diagrams for Zirconia and Zirconia Systems*, the American Ceramic Society, Westerville, OH (1998).



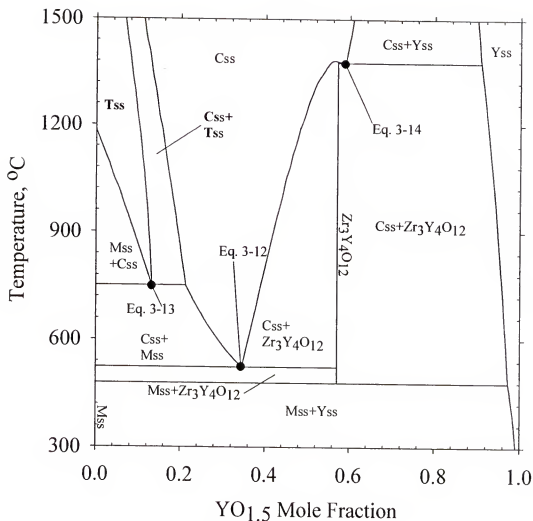
Adapted from: Liang et al. (2001)

Figure 3-2. Calculated phase diagram in the Zr-O system.
 Liang, P., N. Dupin, S. G. Fries, H. J. Seifert, I. Ansara, H. L. Lukas and F. Aldinger, "Thermodynamic Assessment of the Zr-O Binary System," *Z. Metallkd.* **92**, 747-756 (2001).



Adapted from Stubican (1988) and Suzuki (1995)

Figure 3-3. $\text{YO}_{1.5}\text{-ZrO}_2$ experimental phase diagram (Ccss – face-centered cubic solid solution, Mss – monoclinic solid solution, Tss – tetragonal solid solution, Yss – body-centered cubic solid solution, and $\text{Zr}_3\text{Y}_4\text{O}_{12}$ – 3:4 perovskite). Stubican, V. S., "Phase Equilibria and Metastabilities in the Systems $\text{ZrO}_2\text{-MgO}$, $\text{ZrO}_2\text{-CaO}$, $\text{ZrO}_2\text{-Y}_2\text{O}_3$," *Science and Technology of Zirconia III*. N. Y. S. Somiya, H. Yanagida, **24A**, 71 (1988). Suzuki, Y., "Phase Transition Temperature of Fluorite-type $\text{ZrO}_2\text{-Y}_2\text{O}_3$ Solid Solutions Containing 8-44 mol% Y_2O_3 ," *Solid State Ionics*, **81**, 211 (1995).



Adapted from: Fu et al. (1992)

Figure 3-4. $\text{YO}_{1.5}$ - ZrO_2 calculate phase diagram (C_{ss} – face-centered cubic solid solution, M_{ss} – monoclinic solid solution, T_{ss} – tetragonal solid solution, Y_{ss} – body-centered cubic solid solution, and $\text{Zr}_3\text{Y}_4\text{O}_{12}$ – 3:4 perovskite). Source: Du et al. (1992).

Du, Y., Z. Jin and P. Huang, "Thermodynamic Calculation of the ZrO_2 - $\text{YO}_{1.5}$ - CaO Phase Diagram," *CALPHAD*, **16**, 355 (1992).

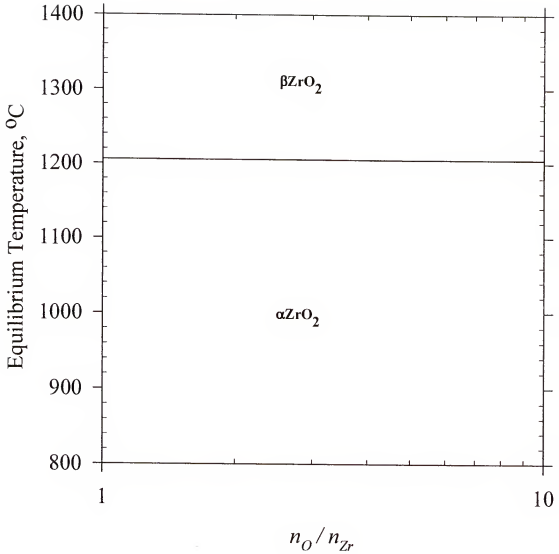


Figure 3-5. CVD diagram as a function of the n_O / n_{Zr} ratio and temperature on solid phase formation. Gas phase not shown here. (Other CVD conditions: $n_H / n_C = 1$, $n_{\text{inert}} / (n_O + n_{Zr} + n_C + n_H + n_{Cl}) = 150$, $2n_C - n_O = 0$, $n_O + n_{Zr} = 0.001$, $n_{Cl} - 4n_{Zr} = 0$, $P = 10^5$ Pa).

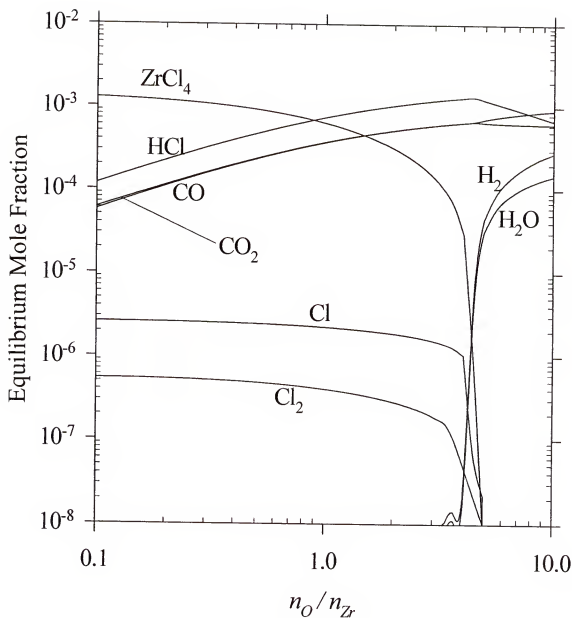


Figure 3-6. CVD diagram showing the effect of the n_O / n_{Zr} ratio on gas phase speciation. (Other CVD conditions: $n_H / n_C = 1$, $n_{inert} / (n_O + n_{Zr} + n_C + n_H + n_{Cl}) = 150$, $2n_C - n_O = 0$, $n_O + n_{Zr} = 0.001$, $n_{Cl} - 4n_{Zr} = 0$, $P = 10^5$ Pa, $T = 1250^\circ\text{C}$). Ar comprises balance of gas phase.

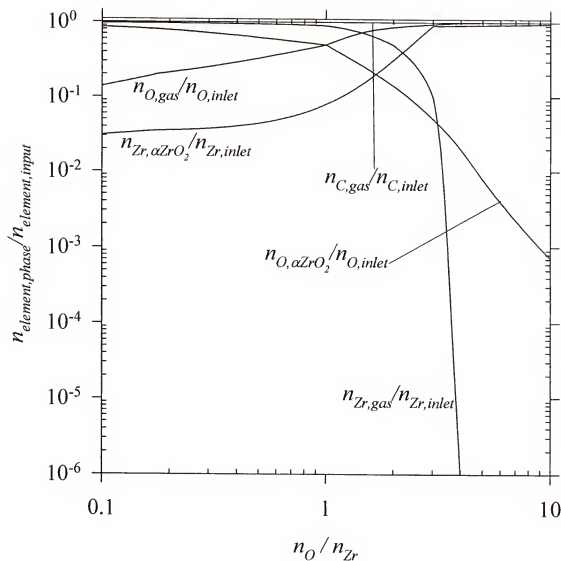


Figure 3-7. CVD diagram showing the effect of the n_O / n_{Zr} ratio on the relative efficiency of phase formation. (Other CVD conditions: $n_H / n_C = 1$, $n_{\text{inert}} / (n_O + n_{Zr} + n_C + n_H + n_{\text{Cl}}) = 150$, $2n_C - n_O = 0$, $n_O + n_{Zr} = 0.001$, $n_{\text{Cl}} - 4n_{Zr} = 0$, $P = 10^5$ Pa, $T = 1250^\circ\text{C}$).

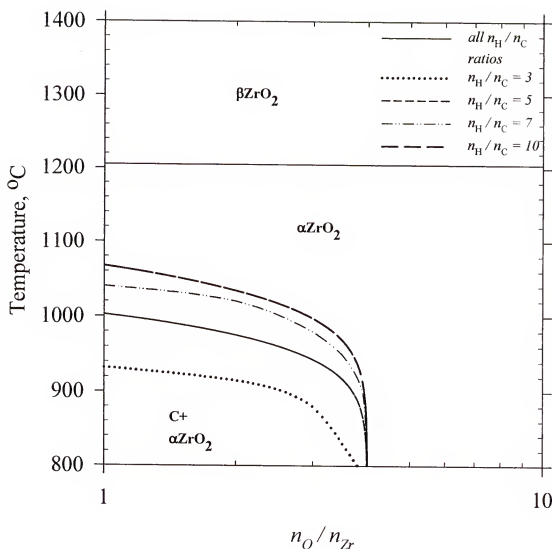


Figure 3-8. CVD diagram showing the effect of the n_O / n_{Zr} ratio and temperature on the phase formation at fixed n_H / n_C ratios. (Other CVD conditions: $n_{\text{Inert}} / (n_O + n_{Zr} + n_C + n_H + n_{Cl}) = 150$, $2n_C - n_O = 0$, $n_O + \underline{n_{Zr}} = 0.001$, $n_{Cl} - 4n_{Zr} = 0$, $P = 10^5$ Pa).

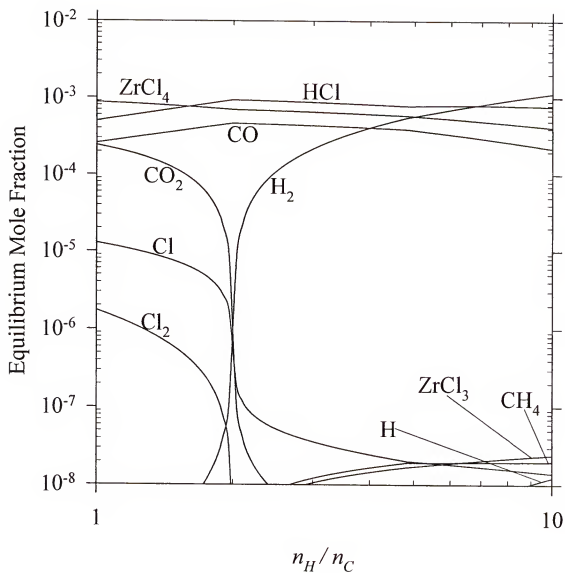


Figure 3-9. CVD diagram showing the effect of the n_H/n_C ratio on gas phase speciation. (Other CVD conditions: $n_O/n_{Zr} = 1$, $n_{Inert}/(n_O + n_{Zr} + n_C + n_H + n_{Cl}) = 150$, $2n_C - n_O = 0$, $n_O + n_{Zr} = 0.001$, $n_{Cl} - 4n_{Zr} = 0$, $P = 10^5$ Pa, $T = 1050^\circ\text{C}$). Ar comprises balance of gas phase.

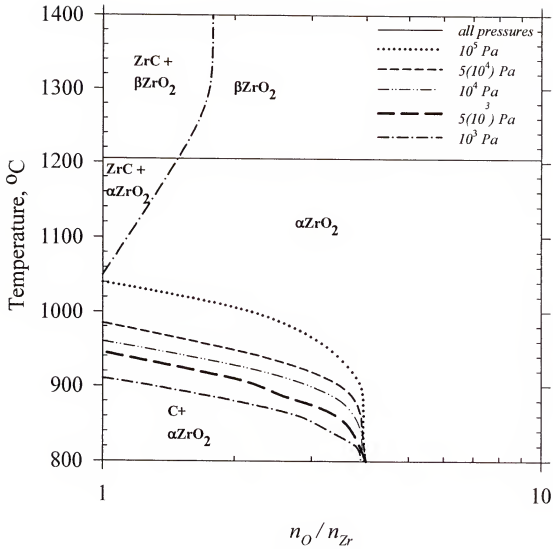


Figure 3-10. CVD diagram showing the effect of the n_O / n_{Zr} ratio and temperature on the phase formation at fixed pressure. (Other CVD conditions: $n_H / n_C = 1$, $n_{Inert} / (n_O + n_{Zr} + n_C + n_H + n_{Cl}) = 150$, $2n_C - n_O = 0$, $n_O + \underline{n_{Zr}} = 0.001$, $n_{Cl} - 4n_{Zr} = 0$).

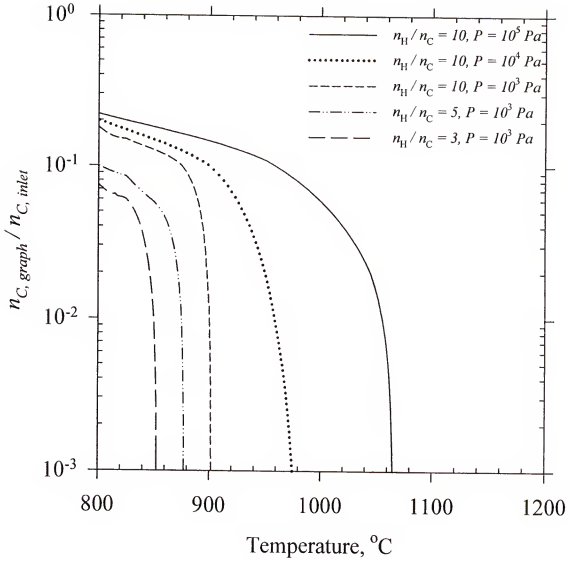


Figure 3-11. CVD diagram showing the effect of temperature on the deposition efficiency of carbon at fixed n_H / n_C ratios and fixed pressure. (Other CVD conditions: $n_{\text{inert}} / (n_O + n_{Zr} + n_C + n_H + n_{Cl}) = 150$, $n_O / n_{Zr} = 1$, $2n_C - n_O = 0$, $n_O + n_{Zr} = 0.001$, $n_{Cl} - 4n_{Zr} = 0$, $P = 10^5 \text{ Pa}$).

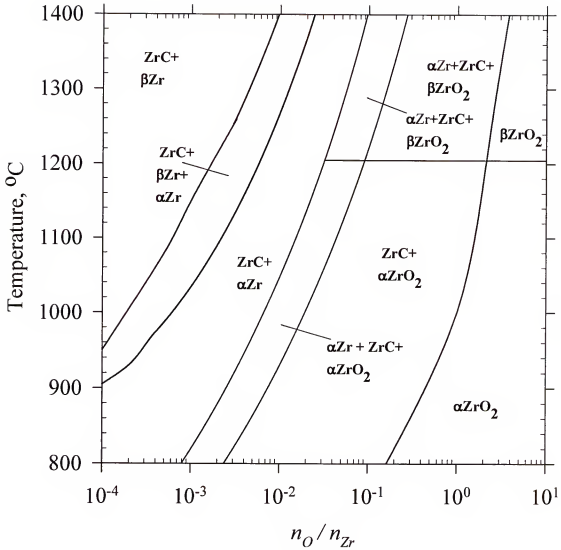


Figure 3-12. CVD diagram showing the effect of the n_O / n_{Zr} ratio and temperature on solid phase formation. Gas phase not shown here. (Other CVD conditions: $n_H / (n_O + n_{Zr} + n_C + n_{inert} + n_{Cl}) = 150$, $n_{inert} / (n_O + n_{Zr} + n_C + n_H + n_{Cl}) = 10^{-20}$, $2n_C - n_O = 0$, $n_O + \underline{n_{Zr}} = 0.001$, $n_{Cl} - 4n_{Zr} = 0$, $P = 10^5$ Pa).

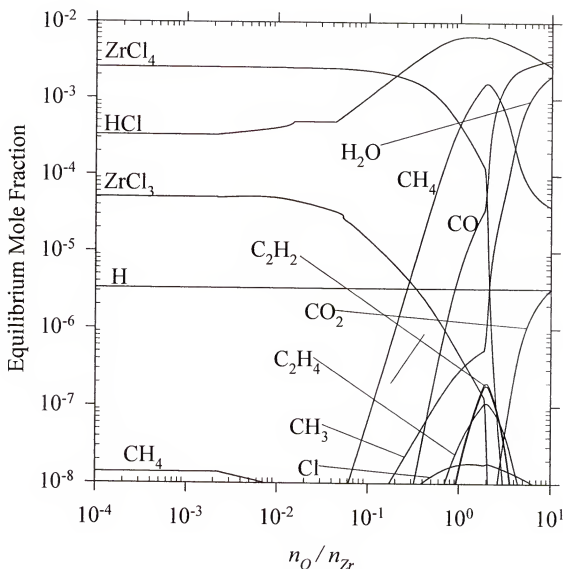


Figure 3-13. CVD diagram showing the effect of the n_O / n_{Zr} ratio on gas phase speciation. (Other CVD conditions: $n_H / (n_O + n_{Zr} + n_C + n_H + n_{Cl}) = 150$, $n_{Inert} / (n_O + n_{Zr} + n_C + n_{Inert} + n_{Cl}) = 10^{-20}$, $2n_C - n_O = 0$, $n_O + n_{Zr} = 0.001$, $n_{Cl} - 4n_{Zr} = 0$, $P = 10^5$ Pa, $T = 1250^\circ\text{C}$). H_2 composes balance of gas phase.

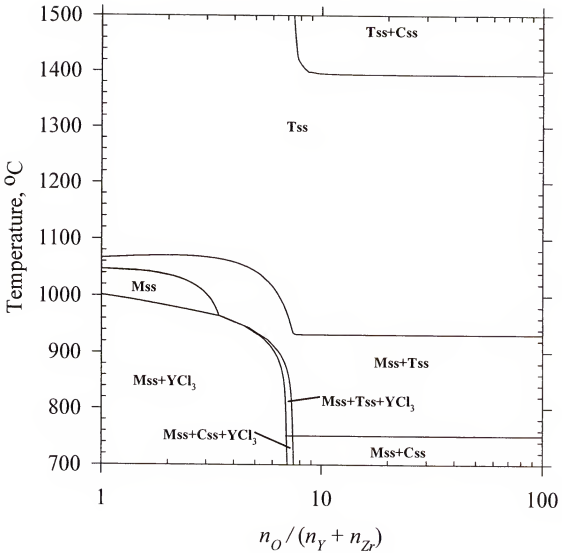


Figure 3-14. CVD phase diagram showing deposited phases as a function of the inlet $n_O / (n_Y + n_{Zr})$ ratio and temperature [inlet CVD conditions: $n_Y / (n_Y + n_{Zr}) = 0.08$, $P = 10^5$ Pa, $n_{Inert} / (n_Y + n_{Zr} + n_O + n_H + n_{Cl} + n_C) = 150$, $n_H / n_C = 1$].

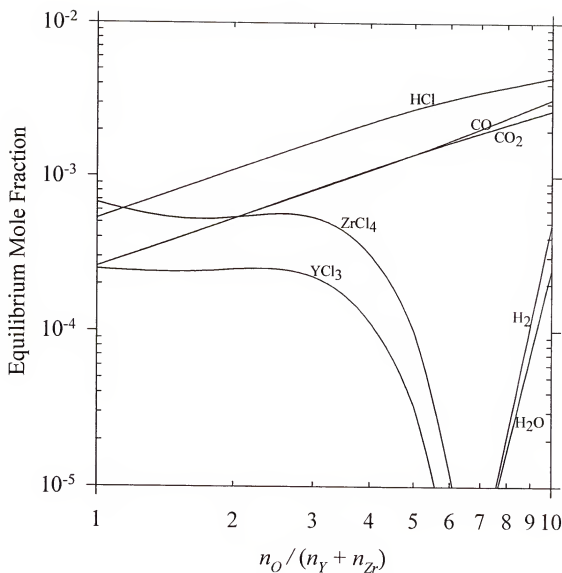


Figure 3-15. Vapor phase equilibrium mole fraction as a function of the inlet $n_O / (n_Y + n_{Zr})$ ratio [inlet CVD conditions: $n_Y / (n_Y + n_{Zr}) = 0.08$, $P = 10^5$ Pa, $T = 1000^\circ\text{C}$, $n_H / n_C = 1$, $n_{\text{inert}} / (n_Y + n_{Zr} + n_O + n_H + n_{Cl} + n_C) = 150$]. Balance of gas phase is inert gas.

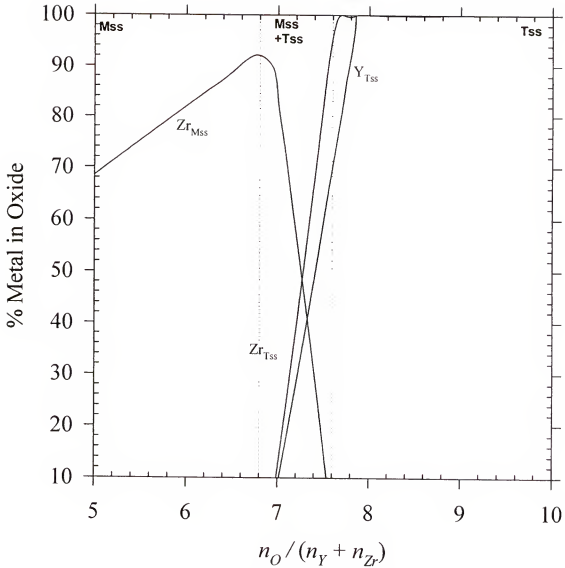


Figure 3-16. Efficiency for deposition as a function of the inlet $n_O / (n_Y + n_{Zr})$ ratio. Here, “Zr, Mss” denotes percent zirconium in the monoclinic YSZ (Mss) phase; “Zr, Tss” denotes percent zirconium in tetragonal YSZ (Tss) phase; and “Y, Tss” denotes percent yttrium in tetragonal YSZ (Tss) phase [inlet CVD conditions: $T = 1000^\circ\text{C}$, $P = 10^5 \text{ Pa}$, $n_{\text{inert}} / (n_Y + n_{Zr} + n_O + n_H + n_{Cl} + n_C) = 150$, $n_Y / (n_Y + n_{Zr}) = 0.08$, $n_H / n_C = 1$].

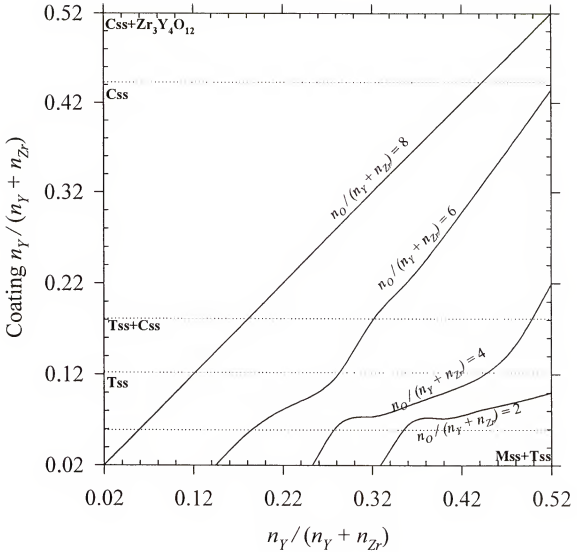


Figure 3-17. CVD phase diagram showing coating composition as a function of the inlet $n_Y / (n_Y + n_{Zr})$ ratio and various inlet $n_O / (n_Y + n_{Zr})$ ratios [inlet CVD conditions: $T = 1000^\circ\text{C}$, $P = 10^5 \text{ Pa}$, $n_{inert} / (n_Y + n_{Zr} + n_O + n_H + n_{Cl} + n_C) = 150$, $n_H / n_C = 1$].

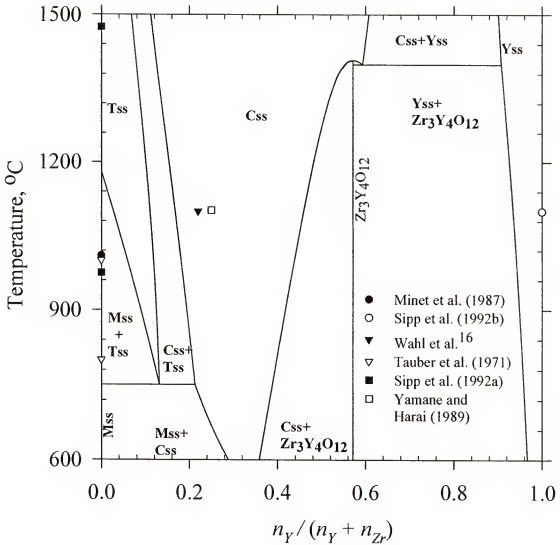


Figure 3-18. Computed CVD phase diagram showing phase deposition as a function of temperature and the inlet $n_Y / (n_Y + n_{Zr})$ ratio [inlet CVD conditions: $P = 10^5$ Pa, $n_O / (n_Y + n_{Zr}) = 8$, $n_{Inert} / (n_Y + n_{Zr} + n_O + n_H + n_{Cl} + n_C) = 150$, $n_H / n_C = 1$]. The data points shown in this figure represent the experimental results obtained by the referred authors, with the experimental conditions given in **Error! Reference source not found.** The phases observed match the phases predicted to form in this work.

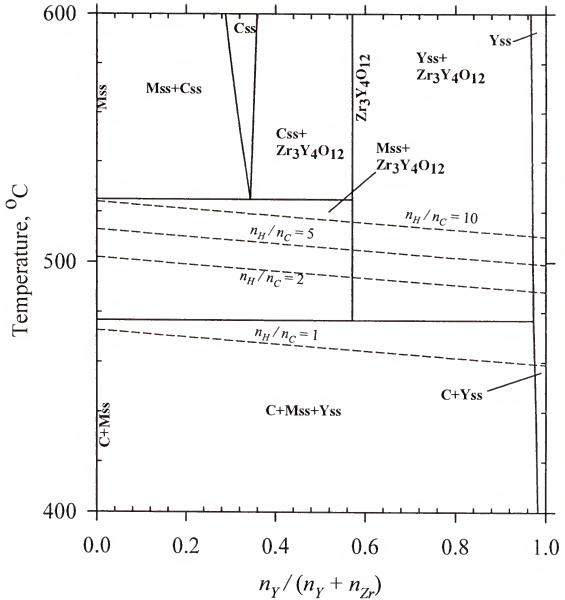


Figure 3-19. CVD phase diagram showing carbon formation as a function of the inlet $n_Y / (n_Y + n_{Zr})$ ratio and the temperature at various inlet n_H / n_C ratios. Here, condensed phase carbon is present at temperatures below those indicated by the dashed lines [inlet CVD conditions: $P = 10^5$ Pa, $n_O / (n_Y + n_{Zr}) = 8$, $n_{inert} / (n_Y + n_{Zr} + n_O + n_H + n_{Cl} + n_C) = 150$].

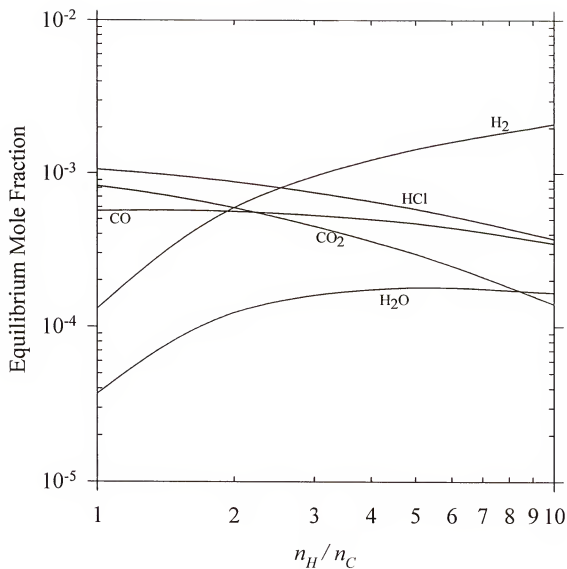


Figure 3-20. Vapor phase equilibrium mole fraction as a function of the inlet n_H / n_C ratio [inlet CVD conditions: $T = 500^\circ\text{C}$, $P = 10^5$ Pa, $n_Y / (n_Y + n_{Zr}) = 0.08$, $n_{\text{inert}} / (n_Y + n_{Zr} + n_O + n_H + n_{Cl} + n_C) = 150$, $n_O / (n_Y + n_{Zr}) = 8$]. Balance of gas phase is inert gas.

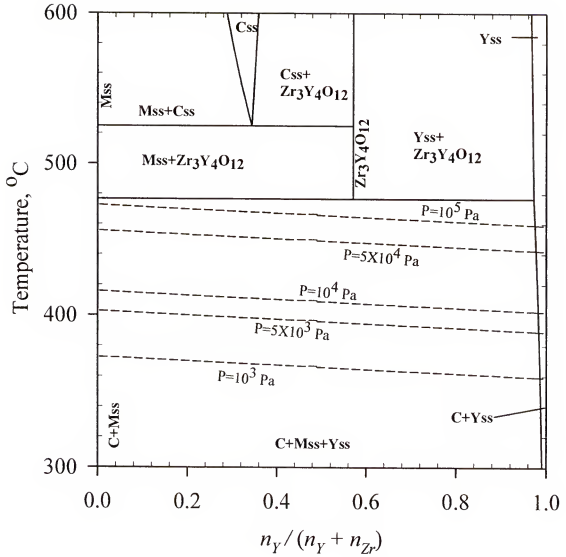


Figure 3-21. CVD phase diagram showing carbon co-deposition boundaries at various values of total pressure. Here, condensed phase carbon is present at temperatures below those indicated by the dashed lines [inlet CVD conditions: $n_O / (n_Y + n_{Zr}) = 8$, $n_H / n_C = 1$, $n_O / (n_Y + n_{Zr}) = 10$, $n_{inert} / (n_I + n_{Zr} + n_O + n_H + n_{Cl} + n_C) = 150$].

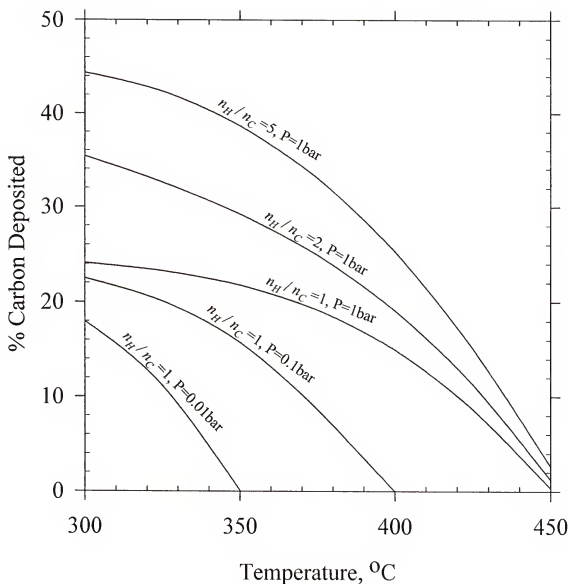


Figure 3-22. Percentage of carbon that co-deposits as a function of temperature and various values of total pressure and inlet n_H/n_C ratio [inlet CVD conditions $n_O/(n_Y + n_{Zr}) = 8$, $n_Y/(n_Y + n_{Zr}) = 0.08$, $n_{Inert}/(n_Y + n_{Zr} + n_O + n_H + n_{Cl} + n_C) = 150$].

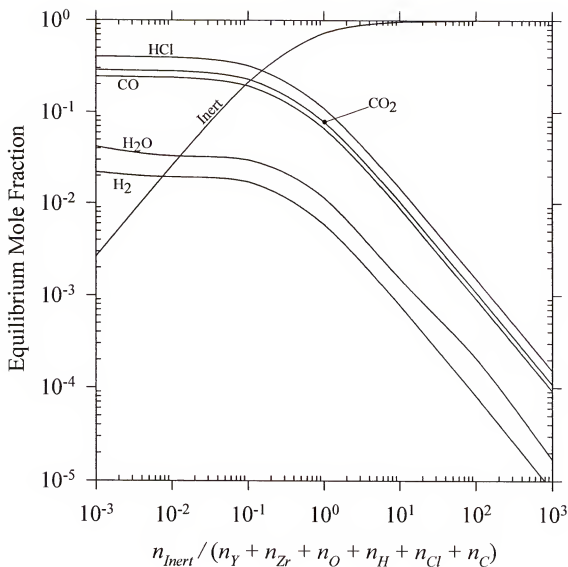


Figure 3-23. Vapor phase equilibrium mole fraction as a function of the inlet $n_{Inert} / (n_Y + n_{Zr} + n_O + n_H + n_{Cl} + n_C)$ ratio [inlet CVD conditions: $T = 1000^\circ\text{C}$, $P = 10^3 \text{ Pa}$, $n_O / (n_Y + n_{Zr}) = 8$, $n_Y / (n_Y + n_{Zr}) = 0.08$, $n_H / n_C = 1$].

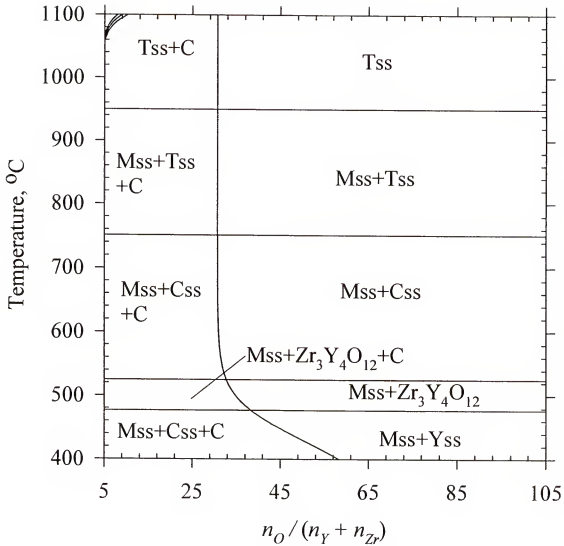


Figure 3-24. CVD diagram showing the effect of the $n_O / (n_Y + n_{Zr})$ ratio and the substrate temperature on solid phase formation. (Other CVD conditions: $n_Y / (n_Y + n_{Zr}) = 0.08$, $P = 10^3$ Pa, $n_C - 21.2n_{Zr} - 126.8n_Y = 0$, $n_H - 48.9n_{Zr} - 158.2n_Y = 0$, $n_{Zr} + n_Y = 0.001$). The thermochemical system at $n_O / (n_Y + n_{Zr}) = 5$ represents the precursor solution introduced to the system without additional molecular oxygen.

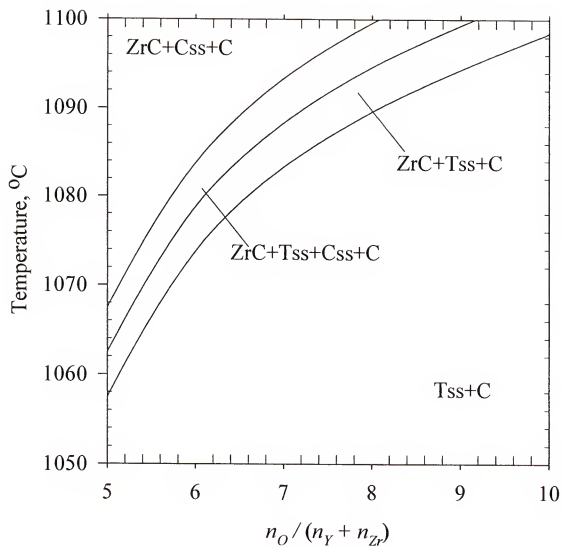


Figure 3-25. Enlargement of upper-left-hand corner of Figure 3-24.

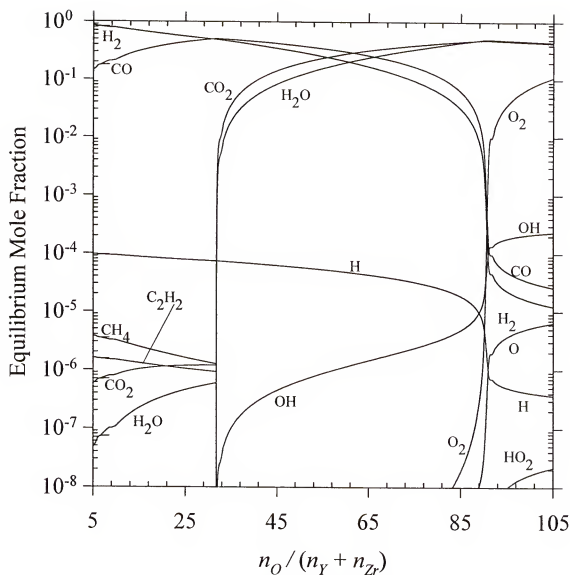


Figure 3-26. CVD diagram showing the effect of the $n_O / (n_Y + n_{Zr})$ ratio on the gas phase speciation at 1100°C. (Other CVD conditions: $n_Y / (n_Y + n_{Zr}) = 0.08$, $P = 10^3$ Pa, $n_C - 21.2n_{Zr} - 126.8n_Y = 0$, $n_H - 48.9n_{Zr} - 158.2n_Y = 0$, $n_{Zr} + n_Y = 0.001$).

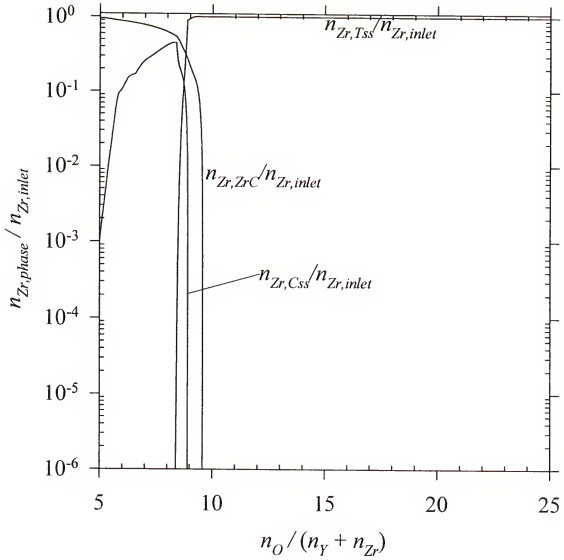


Figure 3-27. CVD diagram showing effect of the $n_O / (n_Y + n_{Zr})$ ratio on solid phase formation at 1100°C. (Other CVD conditions: $n_Y / (n_Y + n_{Zr}) = 0.08$, $P = 10^3$ Pa, $n_C - 21.2n_{Zr} - 126.8n_Y = 0$, $n_H - 48.9n_{Zr} - 158.2n_Y = 0$, $n_{Zr} + n_Y = 0.001$).

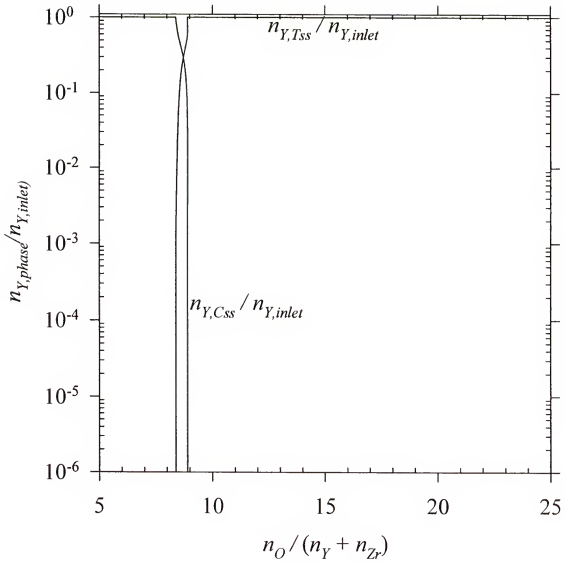


Figure 3-28. CVD diagram showing the effect of the $n_O / (n_Y + n_{Zr})$ ratio on the formation of yttrium-containing phases at 1100°C. (Other CVD conditions: $n_Y / (n_Y + n_{Zr}) = 0.08$, $P = 10^3$ Pa, $n_C - 21.2n_{Zr} - 126.8n_Y = 0$, $n_H - 48.9n_{Zr} - 158.2n_Y = 0$, $n_{Zr} + n_Y = 0.001$).

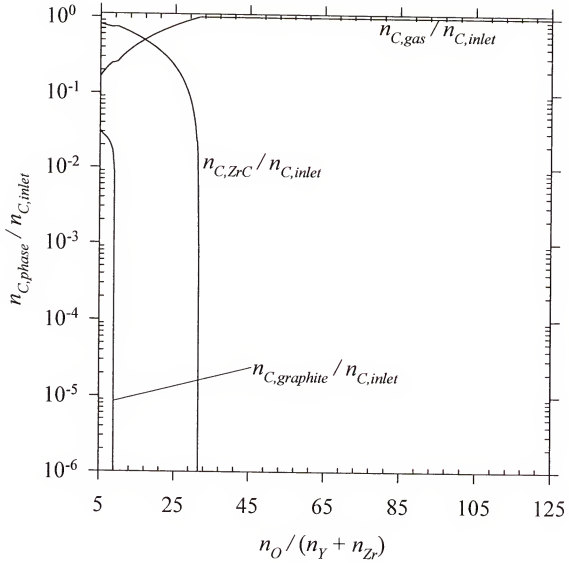


Figure 3-29. CVD diagram showing the effect of the $n_O / (n_Y + n_{Zr})$ ratio on the formation of carbon-containing phases at 1100°C. (Other CVD conditions: $n_Y / (n_Y + n_{Zr}) = 0.08$, $P = 10^3$ Pa, $n_C - 21.2n_{Zr} - 126.8n_Y = 0$, $n_H - 48.9n_{Zr} - 158.2n_Y = 0$, $n_{Zr} + n_Y = 0.001$).

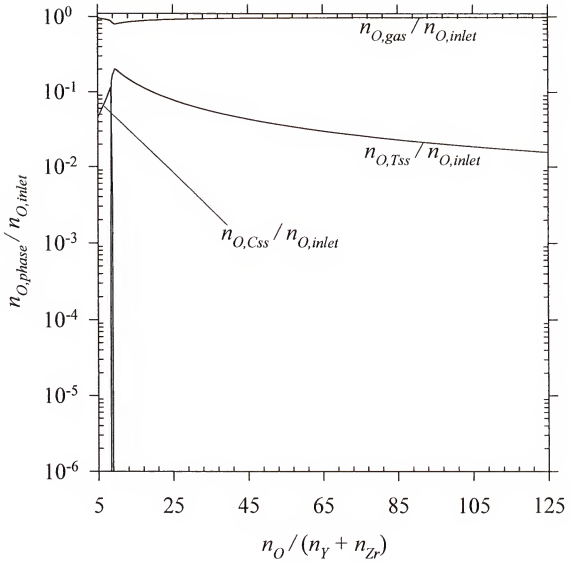


Figure 3-30. CVD diagram showing the effect of the $n_O / (n_Y + n_{Zr})$ ratio on the formation of oxygen-containing phases at 1100°C. (Other CVD conditions: $n_Y / (n_Y + n_{Zr}) = 0.08$, $P = 10^3$ Pa, $n_C - 21.2n_{Zr} - 126.8n_Y = 0$, $n_H - 48.9n_{Zr} - 158.2n_Y = 0$, $n_{Zr} + n_Y = 0.001$).

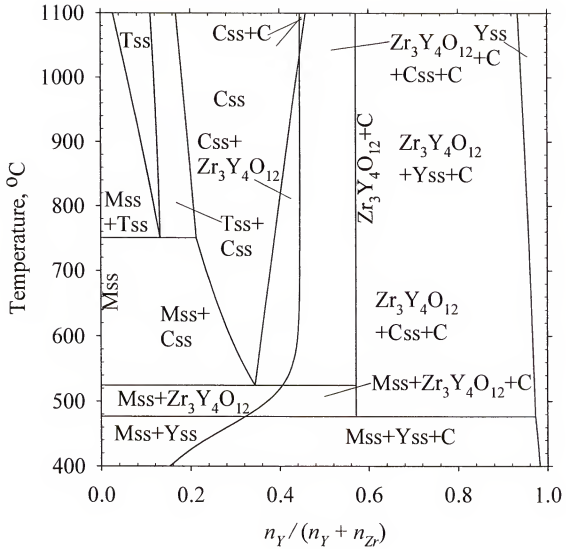


Figure 3-31. CVD diagram showing the effect of the $n_O / (n_Y + n_{Zr})$ ratio and temperature on solid phase formation. Gas phase not shown here. (Other CVD conditions: $n_Y / (n_O + n_{Zr}) = 70$, $P = 10^3$ Pa, $n_C = 21.2n_{Zr} - 126.8n_Y = 0$, $n_H = 48.9n_{Zr} - 158.2n_Y = 0$, $n_{Zr} + n_Y = 0.001$).

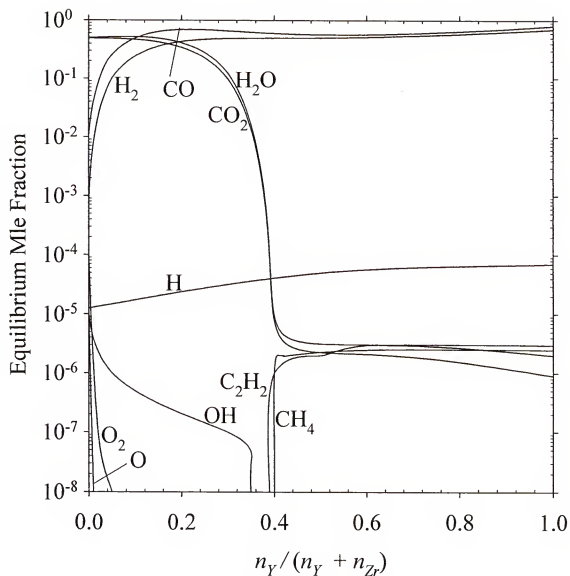


Figure 3-32. CVD diagram showing the effect of the $n_O / (n_Y + n_{Zr})$ ratio on the gas phase speciation at 1100°C. (Other CVD conditions: $n_O / (n_Y + n_{Zr}) = 70$, $P = 10^3$ Pa, $n_C - 21.2n_{Zr} - 126.8n_Y = 0$, $n_H - 48.9n_{Zr} - 158.2n_Y = 0$, $n_{Zr} + n_Y = 0.001$).

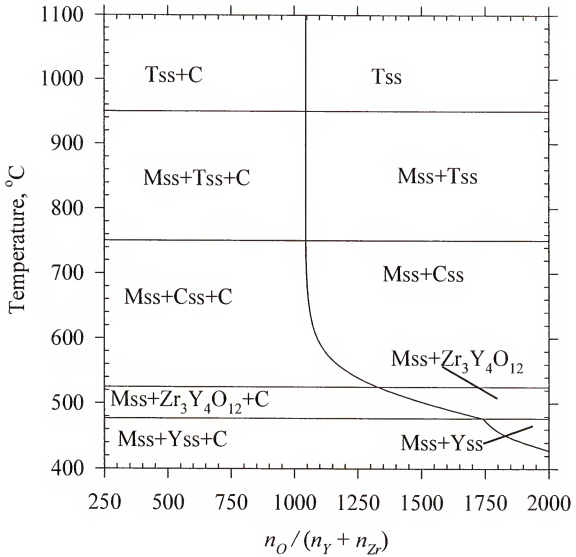


Figure 3-33. Solid phase formation in the Zr-O-Y-C-H system as a function of temperature and $n_O / (n_Y + n_{Zr})$. (Other CVD conditions: $n_Y / (n_Y + n_{Zr}) = 0.08$, $P = 10^3$ Pa, $n_C - 1044n_{Zr} - 10338n_Y = 0$, $n_H - 2076n_{Zr} - 2057n_Y = 0$, $n_{Zr} + n_Y = 0.001$). The thermochemical system at $n_O / (n_Y + n_{Zr}) = 250$ represents the precursor solution introduced to the system without additional molecular oxygen.

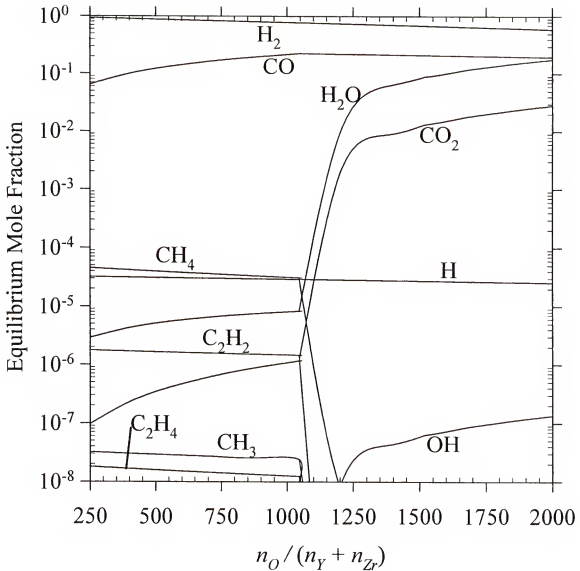


Figure 3-34. Equilibrium gas phase mole fraction of the Zr-Y-O-C-H system as a function of $n_O / (n_Y + n_{Zr})$ at 1000°C. (Other CVD conditions: $n_Y / (n_Y + n_{Zr}) = 0.08$, $P = 10^3$ Pa, $n_C - 1044n_{Zr} - 1033n_Y = 0$, $n_H - 2076n_{Zr} - 2057n_Y = 0$, $n_{Zr} + n_Y = 0.001$). The thermochemical system at $n_O / (n_Y + n_{Zr}) = 250$ represents the precursor solution introduced to the system without additional molecular oxygen.

CHAPTER 4 EXPERIMENTAL APPROACH

This chapter provides on the experimental approach, setup, and analysis tools used for YSZ coating deposition. The details are given for both chloride and metal-organic CVD.

4.1 Materials

The materials used in the reactor include those for the CVD reactor, the aerosol-assisted liquid delivery (AALD) system, precursors, and the substrate and susceptor. The materials used for the CVD reactor are summarized in Table 4-25 and Table 4-26. In the proceeding, please refer to these tables for specific details on these materials.

4.1.1 Reagents

The H₂, CO₂, Ar, O₂, and HCl reagent gases (UHP grade) were supplied by Air Liquide (Oak Ridge, TN), the Zr chips (crystal bar turnings of 99.5% purity) were obtained from Strem Chemicals Inc. (Newburyport, MA).

The Y- and Zr- β -diketonate precursors were Y(tmhd)₃ (99.9%, Alfa-Aesar, Ward Hill, MA) and Zr(tmhd)₄ (99.99%, Alfa-Aesar, Ward Hill, MA) (tmhd = 2,2,6,6-tetramethyl-3,5-heptanedianato) (99.9%, Alfa-Aesar, Ward Hill, MA). These precursors were dissolved in tetrahydrofuran (THF) solvent (99.7+%, Alfa-Aesar, Ward Hill, MA) with a 0.888 g cm⁻³ density.

The Y(OBuⁿ)₃ (99.9+%) and Zr(OBuⁿ)₄ (99.9+%) precursors were provided by Aldrich Chemical, Inc. (Milwaukee, WI). The solutions were 2.23 M Zr in *n*-butanol and

0.5 M Y in toluene. The density of the Zr solution was 0.9 g cm^{-3} and the density of the Y solution was 0.89 g cm^{-3} . The Zr solution was 80 wt. % $\text{Zr}(\text{OBut}^n)_4$ in *n*-butanol and the Y solution was 17.2 wt% $\text{Y}(\text{OBut}^n)_3$ in toluene. The Y- and Zr-*n*-butoxide precursors were already dissolved upon delivery and were approximately one-third of the cost of the Y- and Zr- β -diketonate precursors.

4.1.2 Substrate and Susceptor

The substrates used were α -alumina (99.6% purity, Coors Inc., Oak Ridge, TN) or Rene-N5 (Howmet Research Corporation, Whitehall, MI), and Mar-M247 (Caterpillar, Peoria, IL). The latter two Ni-based super-alloy substrates were Al-rich such that an alumina-scale layer would form during a 10 minute pre-oxidation step. The susceptor was also made of Mar-M247. The Mar-M247 substrates are highly oxidation resistant and can withstand several thousands of thermal cycles below its melting temperature ($\sim 1150^\circ\text{C}$).

4.2 Methods

4.2.1 Pressure and Temperature Control

The substrate temperature control was provided by the following method. The radio frequency (r.f.) generator provided the source of heating. The r.f. generator used induction heating to bring the susceptor to the desired temperature. The radio frequency (r.f.) generator was equipped with a copper coil, which surrounded the CVD chamber wall (Figure 4-1). This coil induced a magnetic field within the reaction zone that induced a potential drop through a metal or graphite work piece, or susceptor. This susceptor was heated (depending on the power output of the r.f. generator) to the desired temperature. The substrate was placed on top of the susceptor to conductively heat the

sample to the desired temperature. The temperature of the susceptor was measured by a k-type thermocouple and verified prior to reaction using an optical pyrometer (calibration in Appendix B).

The pressure was controlled using a capacitance manometer, pressure controller, and a pressure control valve (Table 4-26). The capacitance manometer was placed below the reaction chamber, approximately 15 cm below the substrate region. The pressure was indicated by a pressure controller. Finally, a pressure control valve was used to perform the final control action of pressure regulation.

An oil annulus was used to transport heat away from the inlet gas flow in the stagnation-plane flow design. An oil circulation pump was used with silicone oil as the heat transfer fluid. The oil was brought to temperature of 200°C prior to circulation through the oil annulus.

4.2.2 Precursor Preparation

Precursors for chloride CVD required no initial preparation since they were obtained as Zr chips, which were reacted with HCl gas.

For liquid-delivery, the metal-organic precursors were solvated to make liquid precursor solutions. These liquid precursor solutions were drawn into a syringe for placement onto a syringe pump for accurate liquid delivery. The liquid precursor solutions were prepared in a glove bag to provide an inert atmosphere and minimize precursor exposure to air or moisture. The glove bag was fitted with an Ar inlet tube and a vacuum outlet tube, with each tube connected firmly in place by adhesive tape and vacuum clamps. The glove bag was evacuated using a DuoSeal vacuum pump and Ar back-filled four times to ensure minimal air or moisture content.

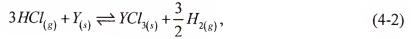
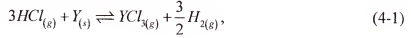
Within the glove bag were the needed supplies for mixing and drawing the precursor solutions into the syringe. To prepare the solution, a 150 ml beaker was placed on top of a magnetically-stirred hot plate. The magnetic stirrer accounted for a 10 ml displacement, thus the solutions were made to 100 ml total volume, of which, and up to 90 ml was drawn into the syringe. Details regarding the precursor solution stoichiometry are given in the chapters to follow. All liquid solutions were prepared in a laboratory, bench-top fume hood.

4.2.3 Precursor Delivery

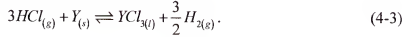
Typically, chloride precursors are introduced to the reaction chamber by precursor sublimation and transported by an inert carrier gas (e.g. Ar, N₂, etc.) (Sipp *et al.* 1992a, Sipp *et al.* 1992b, Minet *et al.* 1987, Wahl *et al.* 1979, Tauber *et al.* 1971, Brennfleck *et al.* 1981). Although simplistic in design, this is an unreliable method of accurately controlling the molar delivery rate of these precursors.

Past workers have noted, however, a difficulty with using YCl_{3(g)} as the yttrium source. Yamane and Harai (1989) and Sipp *et al.* (1992b) attempted atmospheric and low pressure CVD, respectively, to introduce yttrium as a chloride precursor (YCl₃). In these studies, they noted that high temperatures (902–1002°C) were required to vaporize YCl_{3(l)} to obtain YCl_{3(g)} (Yamane and Harai 1989, Sipp *et al.* 1992b). Further, Wahl *et al.* noted difficulties with high temperature chlorination by the reaction of Cl₂ with Y chips in a packed bed reactor (1979). To prevent premature condensation of YCl_{3(g)}, the above authors needed to use a hot-wall CVD reactor. This reactor type is unsuitable due to the possibility of homogeneous nucleation of YSZ on the reactor walls and insufficient growth on the substrate.

Similarly, it was apparent that reaction of yttrium with gaseous hydrogen chloride cannot alleviate this high temperature requirement to form gaseous yttrium tri-chloride. This high temperature requirement is seen in Figure 4-2, which compares the relative favorability of the following reactions:



and



The favorability of these reactions is defined by the change in Gibbs energy (ΔG^o), which is given by,

$$\Delta G^o = \sum_i \nu_i G_i^o(T). \quad (4-4)$$

In Eq. (4-4), ν_i is the stoichiometric coefficient of each species i and $G_i^o(T)$ is the pure component molar Gibbs energy of each species. The term $G_i^o(T)$ is given relative to the enthalpy of its pure elements in their stable element reference state as,

$$G_i^o(T) = G_i(T) - \sum_k n_{ik} H_{ik}^{SER} \quad (4-5)$$

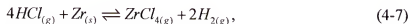
Here, $G_i(T)$ is the temperature dependent molar Gibbs energy of species i , n_{ik} is the moles of element k per mole of species i and H_{ik}^{SER} is the stable element reference enthalpy of each element within species i . As an example, $G_i^o(T)$ for $YCl_{3(g)}$ is given by,

$$G_{YCl_{3(g)}}^o(T) = G_{YCl_{3(l)}}(T) - H_Y^{SER} - 3H_{Cl}^{SER} \quad (4-6)$$

In Eq. (4-6), H_Y^{SER} and H_{Cl}^{SER} are the stable element reference enthalpies for hexagonally close-packed (hcp) yttrium and a $\frac{1}{2}$ mole of Cl_2 gas, respectively, at 298.15 K and 1 bar. In Figure 4-2, it is clear that the reaction to form $YCl_{3(g)}$ is less favored below 1300°C as compared to the reactions to form condensed phases of YCl_3 . The high vaporization temperature, low vapor pressure, and large vapor pressure difference of $YCl_{3(g)}$ as compared to $ZrCl_{4(g)}$ makes reactor design complicated and requires the use of a hot-wall reactor. Thus, yttrium will not be incorporated in chloride CVD, however, zirconia CVD was attempted to determine if high growth rates are achievable.

Before attempting CVD experiments, the Zr chlorinator was evaluated for effective conversion of HCl to $ZrCl_4$ at the desired chlorination temperature. First, the Zr chlorinator was evaluated for the proper heating of flowing precursor gas. Using Ar (30 sccm) as the flowing gas, the temperature of the flowing gas was determined as a function of the distance through the length of the Zr chlorinator. This was accomplished by measuring the thermocouple temperature ($\pm 0.1^\circ C$) from the heating source (heating tape) and from within an empty Zr chlorinator. The Zr chlorinator (stainless-steel tube of 1.91 cm OD, 1.56 cm ID, 30 cm in length) was wrapped in heating tape (VWR, Oak Ridge, TN), which was then wrapped with insulation tape (VWR). An additional thermocouple was wrapped onto the outside of the Zr chlorinator underneath the heating tape to measure the source heating temperature. The thermocouple was placed into the inlet end of the Zr chlorinator and was displaced every 5 cm through the length of the tube until it reached the outlet of the Zr chlorinator.

Next, an assessment of the solid Zr to gaseous ZrCl_4 conversion of the Zr chlorinator was determined to ensure the complete reaction of $\text{HCl}_{(g)}$ with the Zr chips to form $\text{ZrCl}_{4(g)}$,



Ideally, the conversion of HCl to ZrCl_4 should be 0.25 since 4 moles of HCl are required to produce 1 mole of ZrCl_4 . By ensuring this reaction goes to completion, the flow rate of ZrCl_4 into the reaction chamber can be controlled by the flow rate of HCl into the Zr chlorinator. The Zr chlorinator was isolated from the chamber. The heated effluent gas line from the Zr chlorinator was connected to an ice-water cold trap. Based on the vapor pressure curve for $\text{ZrCl}_{4(g)}$ (Figure 4-3), the Zr chlorinator was tested at three different temperatures (300, 380, and 450°C) to evaluate this conversion. An initial mass of Zr was weighed before and the remaining Zr was weighed after experiments to measure the weight loss of Zr due to reaction with HCl and volatilization of ZrCl_4 .

For CVD experiments, the oxidizing reagent gas mixture of H_2 and CO_2 , was metered into the chamber through a separate gas line. This was done to prevent premature reaction with the chloride precursors. Finally, a carrier gas was metered into the reactor to assist reagent transport to the reaction zone. A schematic of this precursor delivery system is provided in Figure 4-4 and details regarding the reagent delivery equipment specifications are provided in Table 4-25.

In the case of MOCVD, the sublimation method is unreliable due to the low precursor vapor pressures and lack of reproducibility in transporting these precursors to the substrate (Chiang *et al.* 1993). In this work, direct liquid injection was used to accurately meter the well-mixed precursor solution of known stoichiometry. The

precursor solution is composed of the solute metal-organic reagents dissolved into a known solvent.

Liquid-delivery has several requirements, particularly pertaining to the solvent. First, the solvent must readily dissolve but not decompose the precursor (Chiang *et al.* 1993). Second, the solvent must easily separate from the metal center of the metal-organic either in the gas phase or on the surface (Chiang *et al.* 1993). This will aid in minimizing impurity incorporation in the coating (Chiang *et al.* 1993). Third, the solvent must not decompose at the substrate surface or in the near-substrate region (i.e. chamber wall), otherwise, contamination may occur within the coating (Chiang *et al.* 1993). In reality, the solvent may decompose due to the possibly high substrate and susceptor temperatures. Ideally, it is desired that the solvent enhance the coating growth rate by enhancing precursor transport to the substrate without getting involved in the growth mechanisms (Chiang *et al.* 1993). As an example, Pilkington *et al.* (1992) and Zheng *et al.* (1992) observed a copper deposition increase when they dissolved their β -diketonate precursor (copper hexafluoroacetylacetonate) in ethanol or 2-propanol.

For efficient precursor volatilization, an ultrasonic atomizer was placed in-line between the liquid-delivery system and the reaction chamber. The ultrasonic atomizer introduced the precursor solution as a fine mist of droplets, or “aerosol,” which was rapidly volatilized and transported by a carrier gas to the substrate. The carrier gas temperature was set above the volatilization temperature of the precursors. This *in situ* aerosol-assisted liquid delivery (AALD) system was simple and added almost no complexity to the reactor design. A schematic of the AALD system is provided in Figure 4-5 and details regarding specifications are provided in Table 4-25.

4.3 Reaction Chamber

In general, CVD reactors are either hot-wall or cold-wall. On one hand, a hot wall reactor uses a wall temperature that is very near the substrate temperature (Haynes *et al.* 2001, Pulver *et al.* 2000, Minet *et al.* 1987, Sipp *et al.* 1992a). This type of reactor was disadvantageous in CVD due to the precursor depletion issues described earlier (Pulver *et al.* 2000, Park 2001), which led to minimize growth rates. On the other hand, a cold wall reactor is ideal for maximizing growth rates since the substrate temperature is higher than the nearby reactor wall temperature and enhances precursor utilization in the near-substrate region.

Typically, vertical, cold-wall CVD chambers employ an axisymmetric gas flow profile (Figure 4-6). In this type of gas flow profile, the axial component of the gas flow velocity is dependent on the radius of the chamber wall due to stagnation points at the gas-chamber wall interface. This follows the assertion that the chamber wall is impermeable to gas flow; this assertion holds since the chamber wall was constructed of quartz.

The gas flow as it approaches the substrate exhibits a single stagnation point at the centerline of flow at the gas-substrate interface. This stagnation point also reaches the center point of the substrate diameter as long as the substrate is concentrically aligned with the chamber wall. Although the velocity, temperature, and concentration profiles are dependent on the radial direction, the coating growth can be relatively uniform as long as the substrate is heated uniformly and the substrate diameter is relatively small compared to the chamber wall diameter (Holstein 1992). Holstein estimated that a variance of approximately 7°C from the substrate center to the substrate edge may occur

at the gas-substrate interface (1992). In a mass-transfer limited regime, such a small temperature variance does not play a significant role in the coating uniformity or growth.

To enhance growth uniformity, a stagnation-plane flow design was implemented (Figure 4-7) (Gadgil 1992, Kleijn *et al.* 1996, Van Santen *et al.* 2000). The stagnation-flow design distributes the laminar flow profile ($v_z(r)$) of the incoming coating gas mixture such that the velocity (v_z), temperature (T), and reagent concentration (c_i) profiles are uniform in the radial direction (r) as the gas stream approaches the substrate (Houtman *et al.* 1986),

$$\frac{\partial}{\partial r}(v_z, T, c_i) \rightarrow 0. \quad (4-8)$$

The tangential component (θ) of the incoming gas flow, temperature, and reactant concentration were assumed non-existent since the substrate does not spin and the flow profile is assumed axisymmetric (Dandy *et al.* 1997):

$$\frac{\partial}{\partial \theta}(v, T, c_i) \rightarrow 0. \quad (4-9)$$

Further, the substrate was uniformly heated (in the radial direction) by conduction from an inductively heated susceptor (Meiners and Hemmerlman 1993). Thus, all surface reactions were assumed to occur at the same temperature over the substrate diameter. Ideally, the coating thickness grows in the reverse-axial-flow direction (z) (perpendicular to the substrate plane) with near-uniform cross-section. To further ensure uniformity, substrates with a diameter less than the incoming bulk gas flow diameter were used (Dandy *et al.* 1997). The approximate solution to this boundary-layer problem was not approached in this work as this is well-known (White 1991, Bird *et al.* 1960, Schlichting *et al.* 1999).

4.3.1 Effect of Geometry

As described above, the geometry in a CVD reactor can have an impact on the gas flow profile. In axisymmetric flow, the chamber wall causes the gas flow properties (v , T , C_A) to be dependent on the chamber radius. According to Bird *et al.* (1960), the radial dependence of the gas flow properties are less pronounced near the centerline of flow. This means the gas entering the near substrate region is fairly uniform in its gas flow properties so long as the substrate diameter is sufficiently small relative to the chamber wall inner diameter (Fotiadis and Kieda 1990).

In stagnation-plane flow, the effect of the chamber wall is not as significant. This is due to the close proximity (within 1 cm vertical space) of the inlet gas flow relative to the substrate (Holstein 1992). However, recirculation and edge effects can be problematic in this type of geometry due to inlet and/or substrate/susceptor geometry (Holstein 1992). Thus, it is imperative that the substrate and/or susceptor diameter be equal or smaller than the inlet gas flow diameter (Holstein 1992).

Another geometrical effect, the boundary layer, influences growth efficiency. The boundary layer is a layer in which reagents must diffuse through to arrive at the surface for reaction. This boundary layer can account for the large inefficiency in most CVD reactors. In most vertical, cold-wall CVD chambers, the boundary layer must be thinned such that the mass-transfer resistance of this layer is diminished (Pierson 1992). If the boundary layer is too large, the growth rate efficiency becomes low (Holstein 1992, Fotiadis and Kieda 1990). Subsequently, reactants are lost because they are swept away by forced convection and transported away from the substrate. The reactants can then react or re-condense further downstream.

4.3.2 Effect of Gas Flow and Substrate/Chamber Heating

Recirculation of gas flow is an issue in axisymmetric and stagnation-point flow reactors. Recirculation is the phenomenon in which the gas flow above the substrate “rolls”. This rolling is characterized by a circular-like pattern to the gas flow. If this recirculation is near the substrate, much of the gas flow (and subsequently, much of the reactants) can be swept away from the substrate. This recirculation is caused by the forced convective gas flow being counteracted by the natural convective gas flow, owed to substrate heating and subsequent thermal buoyancy (Fotiadis and Kieda 1990, Holstein 1992). In essence, recirculation causes the boundary layer to thicken and increases the mass-transfer resistance to reactant diffusion. Recirculation can lead to homogeneous nucleation and significant reactor wall deposition (Holstein 1992, Fotiadis and Kieda 1990). Thus, recirculation of the gas flow must be avoided to ensure high growth efficiency (> 20%) (Fotiadis and Kieda 1990, Holstein 1992).

Recirculation and growth rate efficiency are dependent on the inlet gas flow velocity (v) and substrate temperature (T) (Fotiadis and Kieda 1990). The optimization of these two factors leads to boundary layer thinning (Holstein 1992). The boundary layer, in general, can be thinned as long as the gas flow velocity is sufficient and the difference in the substrate and gas flow temperatures is not too large (Pierson 1992, Park 2001).

The effect of the gas flow velocity is represented by the Reynolds number as,

$$Re = \frac{\rho v D}{\mu}, \quad (4-10)$$

where ρ is the gas density, μ is the gas viscosity, and D is the inlet gas flow diameter in a cylindrical tube for axisymmetric flow or the length scale (L) between the inlet gas flow and the substrate in stagnation-plane flow. This Reynolds number physically represents

the ratio of the free stream gas flow to the resistance of that free stream gas flow due to surface tension at an impermeable surface, such as a chamber wall or substrate (Bird *et al.* 1960). When the Reynolds number becomes large, forced convection towards the substrate becomes large. Thus, increasing the inlet gas flow velocity can increase the Reynolds number such that forced convection to the substrate is high.

Substrate heating causes thermal buoyancy, which leads to natural convection of the gas flow away from the hot substrate. This thermal buoyancy is represented by the Grashof (Gr) number,

$$\text{Gr} = \frac{\rho^2 g L^3 \left(T^{\text{substrate}} - T^{\text{inlet}} \right)}{\mu^2 T_M}. \quad (4-11)$$

In Eq. (4-11), ρ is the gas density, g is the gravitational constant, L is the characteristic length scale, $T^{\text{substrate}}$ is the substrate temperature, T^{inlet} is the inlet gas temperature, μ is the gas viscosity, and T_M is the mean temperature of the substrate and the inlet gas.

When the Grashof number becomes large, natural convection away from the substrate due to thermal buoyancy becomes large. Thus, decreasing the temperature difference between the inlet gas and the substrate and reducing the inlet-to-substrate distance can reduce the Grashof number such that thermal buoyancy and natural convection away from the substrate is low.

The balance of these forces affects the thickness of the boundary layer. This is best represented as the ratio of the Grashof number to the square of the Reynolds number,

$$\frac{\text{Gr}}{\text{Re}^2} = \frac{gL}{v^2 T_M} \left(T^{\text{substrate}} - T^{\text{inlet}} \right). \quad (4-12)$$

When Gr/Re^2 is high (> 1), thermal buoyancy has a greater effect on the gas flow in the near-substrate region (Holstein 1992). This means that natural convection away from the

substrate dominates, causing the boundary layer to thicken (Fotiadis and Kieda 1990). When the boundary layer thickens, the gas flow recirculates and causes the coating efficiency to be low (Holstein 1992, Fotiadis and Kieda 1990). If Gr/Re^2 is low (< 1), then convective mass transfer dominates, the boundary layer thins, and the reaction process becomes more efficient (Holstein 1992, Park 2001, Fotiadis and Kieda 1990, Pierson 1992).

4.3.3 Effect of Chamber Pressure

With the above consideration, the effect of pressure can influence the mass-transfer to the substrate. As discussed in Chapter 2, the lowering of pressure can raise the growth rate. The reduction of pressure increases the diffusivity of precursors to the substrate. For example, if the pressure is reduced by a factor of 10, the reagent diffusivity is increased by a factor of 10. Since the diffusivity is increased, the boundary layer thins.

According to Fotiadis and Kieda, the effect of pressure was also reflected in the ratio Gr/Re^2 . (1990) In their transport modeling effort, Fotiadis and Kieda found that Gr decreased with the square of decreasing pressure, while the Reynolds number remained constant. They mention that the decrease in Gr/Re^2 was due to the increased reagent diffusivity, which reflected the greater flux of reagents to the surface. Thus, the effect of thermal buoyancy becomes relatively small compared to the effect of forced convection.

The decreased pressure was also calculated to enhance growth uniformity and decrease homogeneous nucleation (Fotiadis and Kieda 1990). The decreased pressure minimizes recirculation above the substrate, due to the diminished thermal buoyancy (Fotiadis and Kieda 1990). With diminished thermal buoyancy, diffusion of reactants is

homogenous over the substrate diameter, thus promoting almost perfect growth uniformity. (Fotiadis and Kieda 1990)

Contrary to the above discussion, Pierson offers some advantages to using atmospheric pressure as opposed to reduced pressure. (1992) On one hand, the reactor design is simplified since there is no requirement for vacuum pumps. Second, the simplified design reduces costs significantly. Finally, more frequent experiments can be performed using atmospheric pressure. Thus, an optimization of pressure is necessary for most CVD reactors. (Pierson 1992) Thus, the optimization of the reactor pressure is an important step in achieving the high growth rate efficiency desired in this work.

4.4 Waste and Effluent Handling

The effluent of both chloride and MOCVD were vented into a laboratory ventilation hood. For MOCVD, a liquid nitrogen (Air-Liquide) and 2-propanol (VWR) mixture was used to cool a vacuum trap waste reagent and reaction by-products. The vacuum pressure was controlled using a throttling valve (Kurt J. Lesker) and the vacuum was provided by a high-throughput vacuum pump (Kashiyama single stage screw drive pump, model SD 40 V2, Kashiyama Industry Co., Ltd., Japan). The r.f. generator was supplied by Lepel Inc. (Maspeth, NY) and had a 10 kW power supply. Figure 4-1 is a schematic of the chamber and details regarding dimensions of the CVD chamber are given in Table 4-25.

4.5 Post-Processing

Weight gain measurements were made using a quartz microbalance. The substrates were weighed before and after coatings were deposited. To convert weight gain to growth rate, the following formula was used,

$$r_{dep} = \frac{10000 \cdot m}{t \cdot \rho_{T,t-YSZ} \cdot A_S} \quad (4-13)$$

In Eq. (4-13), r_{dep} is the growth rate in $\mu\text{m h}^{-1}$, m is the mass gain in grams, t is the experimental time in hours, $\rho_{T,t-YSZ}$ is the theoretical density of tetragonal YSZ (6.1 g cm^{-3}), A_S is the substrate surface area in cm^2 , and the factor of 10000 is used to convert from 1 cm to 1 μm . The deposition rate estimated using Eq. (4-13) was then compared to the growth rate as determined by electron microscopy.

If carbon appeared on the coating (giving the coating a black or brownish-black surface color), an additional oxidation step was used to oxidize this carbon by calcining for 4 hours at 1000°C using a high-temperature box furnace (NEY Furnace, model no. 2-525 series II, Tucuma, CA). The samples were then weighed again to determine the amount of surface carbon (if any) on the coating.

4.6 Coating Analysis

Several techniques for analyzing the YSZ coating are needed for qualitative, semi-quantitative, and quantitative analysis. They include x-ray diffraction (XRD) for crystal structure analysis, scanning electron microscopy (SEM) for morphological coating analysis, and electron probe microanalysis (EPMA) for coating compositional analysis.

4.6.1 Coating Crystal Structure Analysis

The specific x-ray method (Bragg-Brentano method) used in this work allowed for the comparison of the relative intensities of the various hkl plane reflections. This comparison was very useful when qualitatively (or semi-quantitatively) determining the preferred orientation, crystallite size, and mole fraction of a two-phase material (if applicable) (Ciosek *et al.* 2003). Thus a Bragg-Brentano method was used for such an

analysis. In this method, the incident and diffracted beam angles, θ , were the same and the angle, 2θ , between the diffracted and transmitted beam was analyzed (Ryu *et al.* 1997, Jenkins and Snyder 1996).

A Scintag PADV room-temperature XRD (RT-XRD) with a vertical theta/2-theta goniometer was used. The Scintag PADV XRD, had a Cu source (45 kV, 40 mA), and Peltier-cooled solid state Si(Li) detector and a radius of 220 mm. The high energy discrimination of the Si(Li) detector eliminated the need for a Ni-foil beta filter. The *DMSNT* (v. 1.37) software package was used to collect data over the range from 5° to 90° 2θ with 0.02 deg steps, at a scanning rate of 1.0 deg min^{-1} . The instrument used a 1 mm divergence slit, 2 mm anti-scatter slit, 0.5 mm receiving anti-scatter slit, and a 0.3 mm receiving slit.

The software package *JADE* (*JADE* 2000) was used to analyze the X-ray data collected by the *DMSNT* software package. The sample pattern was then compared to the PDF cards (ICCD 2002) for tetragonal YSZ, baddelyite (monoclinic zirconia), and corundum (substrate). These PDF cards contained the specific details on peak reflection diffraction angles, orientation, phase identification, etc. Appendix A lists the information regarding these PDF cards. These cards assisted in the qualitative and semi-quantitative analysis of the sample peak broadening.

To analyze sample peak broadening, the procedure outlined by Jenkins and Snyder (1996) and the *JADE* software package will be implemented. When analyzing a sample diffraction pattern, using the full-width at half maximum (*FWHM*) was advantageous in characterizing any peak broadening associated with the sample. The

peak broadening in a sample pattern is comprised of the full-width instrumental broadening ($FW(U)$) and the full width sample broadening ($FW(S)$). Thus,

$$FWHM = FW(I) + FW(S). \quad (4-14)$$

The instrumental broadening was obtained by using the NIST 340A LaB_6 powder standard for powder x-ray diffraction. From the sample pattern obtained, a resultant $FWHM$ was observed; however, this broadening was miniscule. The sample broadening in this LaB_6 powder was simply owed to the instrumental broadening, thus the resulting $FWHM$ becomes $FW(I)$ (JADE 2000). This sample was profile fitted with a known LaB_6 PDF card to obtain the FWHM curve. This FWHM curve was used as a basis to subtract the instrumental broadening from future sample patterns. Thus, $FW(I)$ is defined as,

$$FW(I) = FWHM_{LaB_6} = A + B \cdot (2\theta) + C \cdot (2\theta)^2. \quad (4-15)$$

In Eq. Figure 4-4(4-15), A , B , and C are least squares regression coefficients and 2θ is the diffraction angle for the Bragg-Brentano diffractometer. The sample broadening was defined by the Debye-Scherrer relation,

$$FW(S) = \frac{1}{\cos(\theta)} \left(\frac{K\lambda}{d} + 4\tau \sin(\theta) \right), \quad (4-16)$$

where K is the shape factor for the average crystallite, λ is the wavelength for the $Cu K_{\alpha 1}$ x-ray in nm, d is the average crystallite size in nm, and τ is the micro-strain. The Debye-Scherrer equation is solved for the family of x-ray lines for a sample.

In general, the sample broadening is determined using the following relation,

$$FW(S)^D = FWHM^D - FW(I)^D, \quad (4-17)$$

where D is a deconvolution factor (set to 0 to 2.0). If small crystallites are assumed to be present, then the strain is neglected ($K\lambda/d \gg 4\tau \sin(\theta)$). This means that Eq. (4-16) is simplified to the Scherrer relation and the average crystallite size is estimated by,

$$d = \frac{K\lambda}{FW(S)\cos(\theta)}. \quad (4-18)$$

Once a sample pattern is profile fitted, it is analyzed for the relative abundance of a two-phase material (if necessary). This calculation was performed using the relative intensity ratio method outlined by Jenkins (1989). For a two-phase mixture that is profile fitted with known PDF cards (and hence, has a known reference intensity ratio,

$RIR_{\alpha, standard}$, the weight fraction of phase α , x_α , is given by,

$$x_\alpha = \frac{I_{i,\alpha} \cdot I_{k,standard}^{rel} \cdot x_{standard}}{I_{k,standard} \cdot I_{i,\alpha}^{rel} \cdot RIR_{\alpha,standard}}, \quad (4-19)$$

where $I_{i,\alpha}$ is the intensity of the diffracted peak of phase α , $I_{k,standard}^{rel}$ is the relative intensity of the internal standard diffraction peak (obtained from the PDF card), $x_{standard}$ is the weight fraction of the standard, $I_{k,standard}$ is the intensity of the standard diffraction peak, and $I_{i,\alpha}^{rel}$ is the relative intensity of a diffraction peak for phase α (and can be found in the PDF card). The term, $RIR_{\alpha,standard}$, is the reference intensity ratio for phase α relative to the internal standard for corundum ($\alpha\text{-Al}_2\text{O}_3$) and is given by,

$$RIR_{\alpha,standard} = \left(\frac{I}{I_{corundum}} \right)_\alpha. \quad (4-20)$$

If an additional phase (β) is present, then the weight fraction, x_β , is given by,

$$x_{\beta} = \frac{I_{i,\beta} \cdot I_{k,s \tan dard}^{rel} \cdot x_{s \tan dard}}{I_{k,s \tan dard} \cdot I_{i,\beta}^{rel} \cdot RIR_{\beta,s \tan dard}}, \quad (4-21)$$

where $I_{i,\beta}$ is the intensity of the diffracted peak of phase β , and $I_{i,\beta}^{rel}$ is the relative intensity of a diffraction peak for phase β . Since corundum is a reference standard and only α and β phases exist, then Eq. (4-19) can be divided by Eq. (4-21) to give

$$\frac{x_{\alpha}}{x_{\beta}} = \frac{I_{i,\alpha} \cdot I_{j,\beta}^{rel} \cdot RIR_{\beta,corundum}}{I_{j,\beta} \cdot I_{i,\alpha}^{rel} \cdot RIR_{\alpha,corundum}}. \quad (4-22)$$

Since the sum of all the weight fractions must equal unity, then finding the weight fractions of each phase is relatively simple. For a polycrystalline phase with multiple resolvable and non-overlapping peaks, an optimized weighted average is used for each phase to give more precision for this calculation. Please note that the estimated values for the crystallite size, micro-strain, and phase weight fraction were considered semi-quantitative at best since the values given from the PDF cards are not considered very accurate (Jenkins 1989). If performed consistently, however, these calculations provided a wealth of information with regard to how various CVD process conditions influenced the coating crystallinity.

4.6.2 Coating Morphological Analysis

The electron microscope used in this work was a Hitachi S4700 field-emission secondary electron microscope. (Hitachi, Inc., Japan) This instrument was equipped with an electrostatic beam blanker and a cold cathode field-emission gun with a 1-30 keV accelerating voltage. The magnification capability was 600,000 $\times$ and the resolution was 1.2 nm at this magnification. This instrument was fitted with an x-ray, secondary, backscattered, and transmitted electron detectors. (Hitachi, Inc.)

4.6.3 Coating Compositional Analysis

Electrons probe microanalysis (EPMA), or sometimes known as wavelength dispersive spectroscopy (WDS), was used in measuring the elemental composition in CVD coatings ($> 3 \mu\text{m}$ thick). EPMA uses an incident electron beam to excite a sample and produce x-rays of characteristic energy and wavelength. The EPMA spectrometer analyzes specimens at a range of incident angles such that Bragg's law is satisfied,

$$n\lambda = 2d \sin(\theta) \quad (4-23)$$

Although electron dispersive spectroscopy was an easier tool to employ and was available with the SEM *in situ*, there are several advantages offered by EPMA. (Goldstein *et al.* 1992) First, the EPMA has a resolution of approximately 10 eV as opposed to the EDS resolution of 150 eV. The EPMA resolution made it easier to resolve the Y and Zr family of x-ray lines since these lines differed by as much as 80-120 eV. This means that the resolution of the EDS was considered insufficient for resolving Y and Zr characteristic x-ray lines. In addition, the peak-to-background ratio for the EPMA detector was about 10 times greater than the EDS detector, making it easier to discern characteristic peaks from the continuum background. (Goldstein *et al.* 1992)

Due to the large amount of x-ray lines that were analyzed from the specimen, corrections were made to account for the inter-element (matrix) effects. (Goldstein *et al.* 1992) These matrix effects originate from the phenomenological effects of elastic and inelastic scattering and the propagation of x-rays through the sample to the detector. These matrix effects are classified into effects owed to atomic number (Z), absorption

(A), and fluorescence (F). The product of these correction factors is known as the *ZAF* correction. (Goldstein *et al.* 1992)

The *ZAF* correction is the most accurate method to account for these matrix effects. (Goldstein *et al.* 1992) The *ZAF* correction is performed sequentially for the family of x-ray lines generated from each element, *i*, in a specimen. This correction is used to adjust the weight fraction determination of each element, *i*, in the specimen by the following relation,

$$\frac{C_i}{C_{(i)}} = [ZAF]_i \cdot \frac{I_i}{I_{(i)}}, \quad (4-24)$$

where C_i is the weight fraction of element *i* in the specimen, $C_{(i)}$ is the weight fraction of element *i* in the standard, $[ZAF]_i$ is the correction factor for element, *i*, I_i is the x-ray intensity of element *i* in the specimen, and $I_{(i)}$ is the x-ray intensity of element *i* in the standard. (Goldstein *et al.* 1992) The discussion with regard to the *ZAF* is truncated here as most software packages employ correction factors that are each unique. The work by Goldstein *et al.* (1992) delves into more detail with regard to the intricacies of the *ZAF* correction for EPMA.

The instrument used in this work was a JEOL 8200 electron microprobe analyzer fitted with a LaB₆ field-emission gun, five wavelength spectrometers and an ultra-thin window energy dispersive spectrometer. The instrument had two spectrometers with highly sensitive solid-state detectors and one spectrometer with a highly sensitive piezo-electric crystal detector. The spot size of this instrument was approximately 3 μm. This spot size was used to analyze the coating composition through the coating thickness.

Table 4-1. Materials and Components Used for CVD Reactor Chamber

Component	Dimensions (cm)					material
	Length	Width	Height	Outer Diameter	Inner Diameter	
Chamber wall (Larson Electronic Glass, Livermore, CA)			33	5.0	4.6	Quartz
Substrate			20.3	3.8	3.5	
Bottom support			2.5			
Transition (Larson Electronic Glass, Livermore, CA)			7.5	3.2	2.9	Quartz
Holder support			2.5	3.2	2.9	
Holder			25.4	3.8	3.5	304
Outer tube			25.4	2.9	2.5	Stainless steel
Injector			3.1	0.08	0.12	
Inner tube						
Nozzle tubes						
Upper vacuum coupling (A&N Corporation, Wiliston, FL)						304 Stainless steel
Lower vacuum coupling (A&N Corporation, Wiliston, FL)						304 Stainless steel
Zr chlorinator/Ar preheater (Ridge Valve, Knoxville, TN)	30			1.9	1.6	304 Stainless steel
Gas lines (Ridge Valve, Knoxville, TN)				0.64	0.48	304 Stainless steel
Exhaust tube (Ridge Valve, Knoxville, TN)	2		2	0.95	0.81	304 Stainless steel
Table support (Oak Ridge National Laboratory)	30	30	38			aluminum

Table 4-2. CVD and Supporting Equipment for Experiments

Component	Description & Model no.	Company	Location
Check valve capacitance manometer,	SS-4CA-3KZ MK622 series (0.2–1000 torr), Low-throughput mechanical	Swagelok Kurt J. Lesker	Swagelok CA Livermore, CA
DuoSeal Vacuum pump	vacuum pump model no. 1374B-01, ,	Welch Rierschle Thomas	Skokie, IL
Glove bag	Number 690321	NPS Corporation	Green Bay, WI
Heating tape	Part no.'s 306058 1"W x 4'L,210 watts	Cole-Parmer	Palatine, IL
Hot Plate	Hot plate with magnetic stirrer Part no.A84301-10	Cole-Parmer	Palatine, IL
Mass flow meters, mass flow meter power supply	MKS 1179A series, MKS 247C	Kurt J. Lesker	Livermore, CA
Oil	A-01294-00	Cole-Parmer	Palatine, IL
Oil Mist Eliminator	Alcatel 2002A series	Kurt J. Lesker	Livermore, CA
Oil Recirculator	A-01262-09	Cole-Parmer	Palatine, IL
optical pyrometers	Ultimax UX10 (900–3000°C), Ultimax UX 50P (300–900°C)	Ircon	Niles, IL
Oxidation furnace	-525 series II	NEY Furnace	Tucaipa, California
Pressure controller	MKS651 series Butterfly valve with viton o-ring and motorized	Kurt J. Lesker	Livermore, CA
Pressure control valve	control from pressure controller, model no. QBV15DSQF40 10 kW power supply,	Kurt J. Lesker	Livermore, CA
Radio frequency generator	equipped with copper tube coil (coil diameter 3", 3/8" coil OD)	Lepel, Inc.	Maspeth, NY

Table 4-2. Continued

Component	Description & Model no.	Company	Location
Syringe	Hamilton Gastight #1100 100ml syringe TEFLON® luer lock with slots (TLL w/ slots)	Hamilton Company	Reno, NV
Syringe needle	1/8" OD (11 gauge) 316 stainless-steel part no. 86020	Hamilton Company	Reno, NV
Syringe pump	model no. 74900-20	Cole-Parmer Instruments Co.	Palatine, IL
thermocouple	k-type (chromel-alumel with 304 stainless-steel sheath) model VC-130AT with a 1/2-wavelength, 40 kHz atomizing probe modified with wrench flats, model no. A07292PRB-1	Omega	Stamford, CT
Ultrasonic atomizer	model no. A07292PRB-1	Sonics & Materials, Inc.	Newtown, CT
Vacuum pump for CVD reactor	Single Stage Screw Drive Pump Model SD 40 V2	Kashiyama Industry Co., Ltd.	Nagano 385 Japan

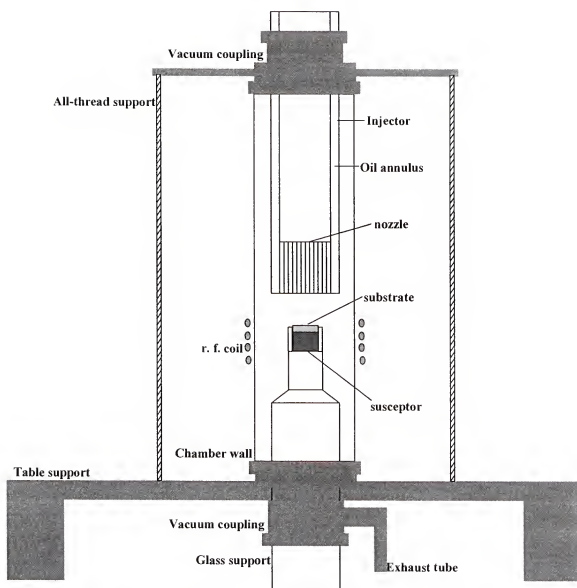


Figure 4-1. Schematic of reaction chamber

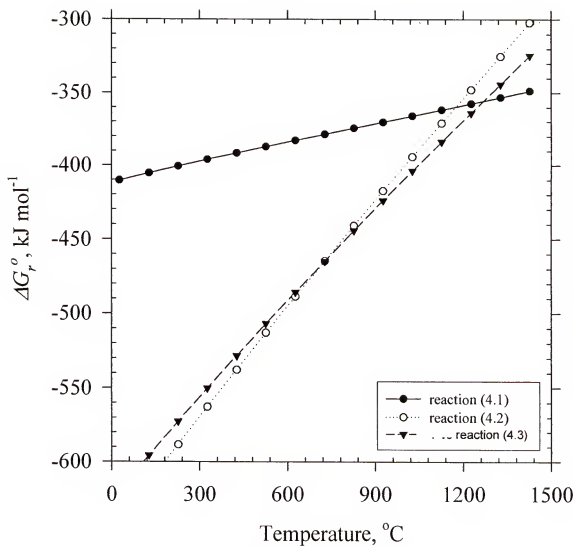


Figure 4-2. Plot illustrating favorable chlorination reactions.

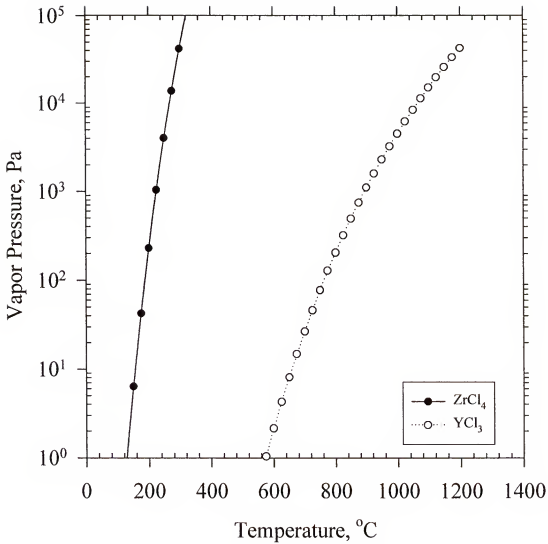


Figure 4-3. Sublimation curves of $\text{YCl}_3(\text{g})$ and $\text{ZrCl}_4(\text{g})$. Adapted from: Shiau, L. F., *Electrochemical Vapor Deposition of Yttria Stabilized Zirconia on Porous Ceramic Substrates* Metallurgical Engineering, University of Illinois, Urbana-Champaign (1993).

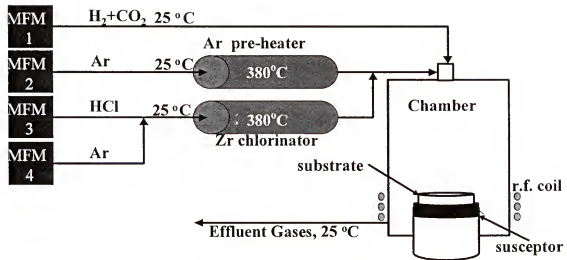


Figure 4-4. Schematic of CVD reactor utilizing *in situ* chlorinator.

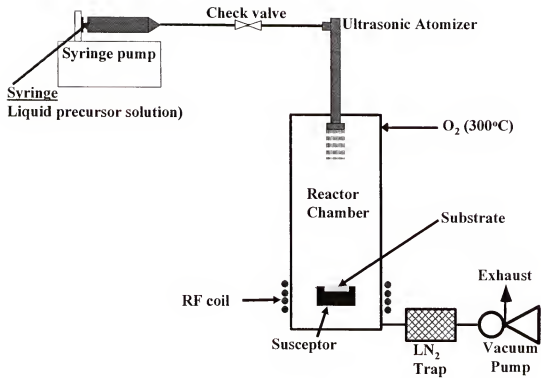


Figure 4-5. MOCVD reactor utilizing aerosol-assisted, precursor liquid-delivery system.

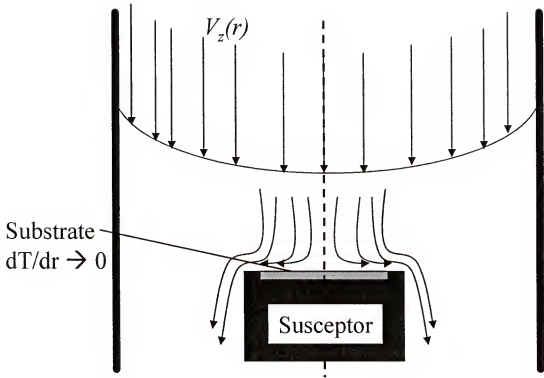


Figure 4-6. Schematic representation of axisymmetric reactor design. *Adapted from:* Holstein, W. L., "Design and Modeling of Chemical Vapor Deposition Reactors," *Progress in Crystal Growth and Characterization*, **24**, 111-211 (1992).

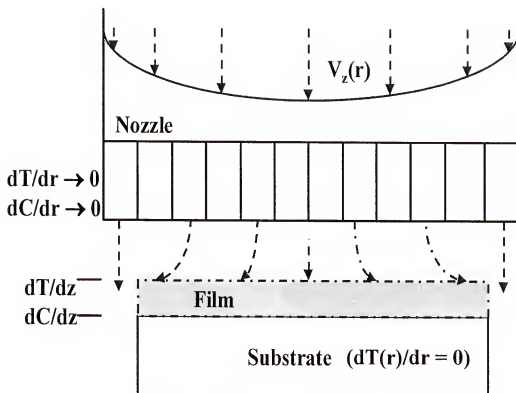


Figure 4-7. Schematic representation of stagnation-plane flow reactor design. *Adapted from:* Gadgil, P. N., "Single Wafer Processing in Stagnation Point Flow CVD Reactor Prospects, Constraints and Reactor Design," *Journal of Electronic Materials*, **22**, 171-177 (1992).

CHAPTER 5 RESULTS AND DISCUSSION OF CHLORIDE CVD

This chapter presented and discussed the results of CVD experiments using metal chloride precursors. The oxygen source was a gas mixture of H_2 and CO_2 , and argon was used as a carrier gas. Results of chlorination studies were also given.

5.1 Results

It was important to determine if the reaction of HCl with Zr was efficient at the desired temperature. This was accomplished by first determining the gas temperature profile through the axial length of the Zr chlorinator. Then, the consumption of Zr by HCl was determined by determining the weight loss of Zr with increasing temperature and a steady flow of HCl..

Shown in Figure 5-1 is the gas temperature profile through the Zr chlorinator. On the horizontal axis is increasing length (z) and on the vertical axis is increasing gas temperature (T). The gas temperature approached the source temperature as the gas flowed through the Zr chlorinator,. The gas temperature profile was observed to increase almost linearly through half ($0.0 < z < 15.0$) of the Zr chlorinator. This gas temperature profile then leveled as the gas flowed to the Zr chlorinator outlet ($15.0 < z < 30.0$). This observation was ideal since the gas temperature at the outlet of the Zr chlorinator could be assumed to be at the source temperature. Thus, the chlorination reaction and the outlet $ZrCl_4$ gas temperature were known and could be controlled.

Next, the experimental consumption of Zr by HCl was determined. This experimental consumption (χ_e) is defined as the ratio of the moles of Zr (n_{Zr}) consumed to the moles of HCl (n_{HCl}) inlet to the Zr chlorinator. Further, the efficiency (χ) of consuming Zr is defined by the ratio of the experimental and theoretical consumption (χ_t) according to Eq. 4.7. This efficiency is given by the following relation:

$$\chi = \frac{\chi_e}{\chi_t} = \frac{(n_{HCl} / n_{Zr})_e}{(n_{HCl} / n_{Zr})_t} = \frac{\left[\frac{Q_{HCl,STP}}{V_{HCl,STP}} t \right] / \left(\frac{\Delta m_{Zr, consumed}}{MW_{Zr}} \right)}{\left(\frac{n_{HCl}}{n_{Zr}} \right)_{Eq.(4.7)}}. \quad (5-1)$$

In the numerator of the far right-hand side of Eq. (5-1), $Q_{HCl,STP}$ is the flow rate (in $\text{cm}^3 \text{min}^{-1}$) of HCl metered at standard temperature and pressure, $V_{HCl,STP}$ is the molar volume (in $\text{cm}^3 \text{mol}^{-1}$) of HCl at standard temperature and pressure, t is the experimental time (in hours), $\Delta m_{Zr, consumed}$ is the weight loss (in grams) of Zr during the chlorination experiment and MW_{Zr} is the molecular weight (in g mol^{-1}) of Zr. In the denominator of the far right-hand side of Eq.(5-1), the quantity $(n_{HCl} / n_{Zr})_{Eq.(4.7)}$ is the stoichiometric ratio (equal to 4) of the moles of HCl to the mole of Zr (n_{Zr}) according to Eq. (4.7).

Prior to reaction, Zr chips were placed into the Zr chlorinator. These chips were weighed and were noted to have a metallic black color. After reaction for two hours in flowing Ar ($20 \text{ cm}^3 \text{min}^{-1}$) and HCl ($10 \text{ cm}^3 \text{min}^{-1}$), the Zr chips were weighed again and were noted to have a greenish-black color. The conversion was then calculated knowing both the flow of HCl and weight loss of Zr after reaction.

The consumption of Zr by HCl was compared to the theoretical conversion given in reaction (4.7). According to reaction (4.7), χ_t should be close to 4. It can be seen that at 302°C , χ was 0.872. This means that 3.45 moles of HCl was used for every mole of Zr

consumed. Thus, more Zr was consumed than was expected according to Eq. (4.7). Nevertheless, the reaction was considered efficient. When the temperature was increased to 380°C and further to 450°C, χ decreased to 0.843 and 0.638, respectively (Table 5-1) with increased consumption of Zr. Again, the conversion at 380°C was considered efficient, however, the conversion at 450°C was considered inefficient.

With knowledge of the ZrCl_4 conversion, CVD experiments were conducted using the optimized thermochemical conditions developed in Chapter 3 (Zr-Cl-O-C-H-Inert system). The conditions and results of experiments are given in Table 5-2. Upon use of these “base” conditions, successful pure metal oxide formation of zirconia was achieved with an estimated growth rate of $2.59 \mu\text{m h}^{-1}$ (run 1, Table 5-2).

Despite the successful deposition of zirconia, increasing other mass-transfer limited parameters did not improve the growth rate significantly and significant powder formation occurred on the reactor walls. When the overall flow rate (Q_{total}) was raised by a factor of three (run 2, Table 5-2), the growth rate increased by approximately one-third to $3.53 \mu\text{m h}^{-1}$. When the inlet CO_2 mole fraction was raised by a factor of two (run 3, Table 5-2), the growth rate increased again by approximately one-third to $4.69 \mu\text{m h}^{-1}$. Finally, when the inlet H_2 mole fraction was raised by a factor of two (run 4, Table 5-2), the growth rate increased by approximately two-thirds to $5.69 \mu\text{m h}^{-1}$. These poor deposition rate increases were also reflected in the growth efficiency by which more ZrCl_4 was consumed to form ZrO_2 . The increase in growth efficiency was desirable; however, the low overall efficiency ($< 1\%$) was inadequate for TBC applications.

Coatings analyzed by XRD showed the deposition to be monoclinic in crystal structure (Figure 5-2 and Figure 5-3). On the horizontal axis is increasing diffraction

angle (2θ), and on the vertical axis is the intensity of the x-ray peak (arbitrary units). Strong characteristic peaks of monoclinic zirconia appeared at 28° and $31.5^\circ 2\theta$. The sample broadening was analyzed by the Scherer formula, which estimated the crystallite size in the coating. The crystallite size estimate for runs 3 and 4 were 40.0 ± 0.9 nm and 54.0 ± 1.1 nm, respectively. This was only a semi-quantitative estimate and does not account for the estimated micro-strain. Micro-strain could not be estimated since distinct singlet peaks were needed at higher angles ($2\theta > 34^\circ$) (Jenkins and Snyder 1996). Peak reflections above $34^\circ 2\theta$ were discernable either due to the difficulty of delineating the substrate from the monoclinic peaks or from the difficulty of delineating doublet peaks of monoclinic zirconia.

The polycrystalline monoclinic zirconia coatings were less than 15 μm in thickness. Electron micrographs of a fracture cross-section of run 4 (Figure 5-4) showed the total growth thickness after two hours of coating to be 10.9 ± 2.19 μm in thickness. This average thickness meant that the growth rate never exceeded $5.5 \mu\text{m h}^{-1}$ and the relatively high standard deviation was due to the rough alumina surface. A 5-volume% HF solution in water was used as a wet-chemical etch to “bring out” the microstructure. This attempt, however, was unsuccessful, perhaps due to an insufficient HF solution concentration. Thus, a specific microstructure was not seen. Finally, the coatings were gray to off-white in color after deposition and no weight change was observed before and after calcine (4 hours at 1000°C in lab air).

Since the coating thickness and growth rate were low, this method was abandoned and further coating studies were halted.

5.2 Discussion

Use of chloride CVD led to the successful deposition of zirconia coatings. These coatings were monoclinic due to the deposition temperature of 1000°C. For tetragonal zirconia growth, the temperature needed to be in excess of 1205°C (Liang *et al.* 2001). It was not feasible to perform deposition at such high temperatures because the maximum use temperature of the deposition equipment was 1050°C.

Experimental results compared reasonably well with the thermochemical results. The experimental conditions used to fabricate monoclinic ZrO₂ were $n_O / n_{Zr} = 25$, $P = 10^5$ Pa, $T = 1000^\circ\text{C}$, and $n_H / n_C = 1, 2$, and 4. These conditions were in reasonable agreement with the thermochemically-optimized conditions ($n_O / n_{Zr} > 4$, $10^3 < P \text{ (Pa)} < 10^5$, $T < 1205^\circ\text{C}$, and $n_H / n_C < 3$) from Chapter 3. In contrast, the efficiency in the thermochemical study was nearly 100%, whereas the efficiency in this chapter was no greater than 1%.

Although successful deposition was demonstrated, the growth rate (and subsequently to deposition efficiency) was insufficient for TBC applications. Similar growth rates were obtained by Wahl *et al.* (1979) and Sipp *et al.* (1992a) (Table 5-2). This low growth rate was further exemplified when the deposition rate did not increase significantly with increasing overall flow rate. Since conversion of HCl to ZrCl₄ was considered efficient and controllable, introduction of ZrCl₄ by this method can be ruled out as the reason for the low growth rates.

The low growth rates and low deposition efficiency may be due to the use of atmospheric pressure. When comparing the pressures used in this work and that of Sipp *et al.* (1992a), it was seen that the pressure in this work was 10^5 Pa and the pressure in

Sipp *et al.* (1002a) was 2×10^3 Pa. As the flow rate was tripled in both this work and Sipp *et al.* (1992a), the growth rate increased by a factor of 5 for Sipp *et al.* (1992a) whereas the growth rate improved by a factor of 1.3 in this work (Table 5-2). According to Pierson (1992), the effect of lowering the reactor pressure (from 10^5 to 10^3 Pa) reduces the mass-transfer resistance of the boundary layer. This lowering of the mass-transfer resistance of the boundary layer occurs because the diffusivity of reagents to the substrate is inversely proportional to the overall reactor pressure (Pierson 1992). This means that reagent transport through the boundary layer (owed to diffusion) increased and, subsequently, the growth rate increased.

The observed powder formation may be associated with the use of atmospheric pressure. This powder formation may have occurred in the gas phase and deposited on the reactor chamber wall. The formation of powders, owed to homogeneous nucleation of the reagents in the gas phase, depleted the amount of reagents that were transported to the substrate (Pierson 1992, Sipp *et al.* 1992a, Sivaram 1995). The formation of powders was increased due to the increased molecular interaction of the reagents at atmospheric pressure as compare to reduced pressure (Pierson 1992, Sivaram 1995). Thus, the low growth efficiency may be owed to the use of an atmospheric pressure reactor.

The experimental consumption of Zr was not only higher than the theoretical consumption (according to Eq. (4.7)); it also increased with increasing temperature. This suggests that the reaction of Zr with HCl may undergo alternative reaction pathways or may have alternative side reactions.

An example of such an alternate reaction pathway or side reactions was found by Shelton (1978) and Copley and Shelton (1970). They found that the lower chlorides of

Zr (ZrCl_3 , ZrCl_2 , and ZrCl) formed above 400°C and pressures between 1 – 5 atmospheres (Shelton 1978). Shelton mentioned that ZrCl_4 gas (a possible product of HCl reaction with Zr) was reduced in the presence of Zr metal (1978). This caused a greenish-black colored surface layer of ZrCl_3 , which was in agreement with Shelton (1978). This layer of ZrCl_3 was relatively involatile as compared to ZrCl_4 (Shelton 1978, Copley and Shelton 1970), and the amount of ZrCl_3 produced increased with increasing temperature (Shelton 1978, Copley and Shelton 1970). Thus, the lower conversion of Zr to ZrCl_4 above 400°C may be due to some moles of Zr converting to surface adsorbed ZrCl_3 .

Table 5-1. Theoretical Versus Experimental Molar Conversion of $\text{HCl}_{(g)}$ to $\text{ZrCl}_4_{(g)}$

Run *	Time (h)	T (°C)	n_{HCl} ** (mol)	Zr			$\chi = \frac{\chi_e}{\chi_i}$
				Initial moles	Final moles	Moles consumed	
1	2	302	0.054	0.404626	0.389279	0.01535	0.872
2	2	383	0.054	0.449572	0.433677	0.01590	0.843
3	2	450	0.054	0.381127	0.360117	0.02101	0.639

* All experiments performed for two hours.

** $n_{\text{HCl}} = Q_{\text{HCl,STP}} / V_{\text{HCl,STP}} \cdot t$

Table 5-2. Comparison of Experimental Results for this Work and Past Researchers.

Run #	Substrate T (°C)	Q_{total} $\text{cm}^3 \text{min}^{-1}$	Mole fraction (y)**			Wt. gain (mg)	Est. growth rate ($\mu\text{m h}^{-1}$)	Eff. ($n_{\text{Zr, coating}} / n_{\text{Zr, inlet}}$)
			H ₂	CO ₂	ZrCl ₄			
1	995	510	0.0196	0.0196	0.0016	8.5	2.59	0.0043
2	1010	1530	0.0196	0.0196	0.0016	11.6	3.53	0.00593
3	1000	1530	0.0196	0.0392	0.0016	15.4	4.69	0.00787
4	1010	1530	0.0392	0.0196	0.0016	19.3	5.87	0.00978
Wahl <i>et al.</i> (1979)	1000	380	$y_{\text{O}_2} = 0.057$ (H ₂ -CO ₂ not used)			0.7×10^3	2.4	0.0040
Minet <i>et al.</i> (1987)	965	475	0.5	0.16	0.016	4×10^3	0.7	0.0004
Minet <i>et al.</i> (1987)	1050	500	0.18	0.06	0.003	2×10^3	3.1	0.0081
Minet <i>et al.</i> (1987)	1050	1500	0.18	0.06	0.003	2×10^3	15.5	0.0405

* Growth time of 2 hours, chlorinator temperature of 382°C, pressure was 10^5 Pa.

** Balance of gas phase composed of Ar. 20 sccm of Ar flow diverted to Zr chlorinator to assist in ZrCl_{4(g)} transport.

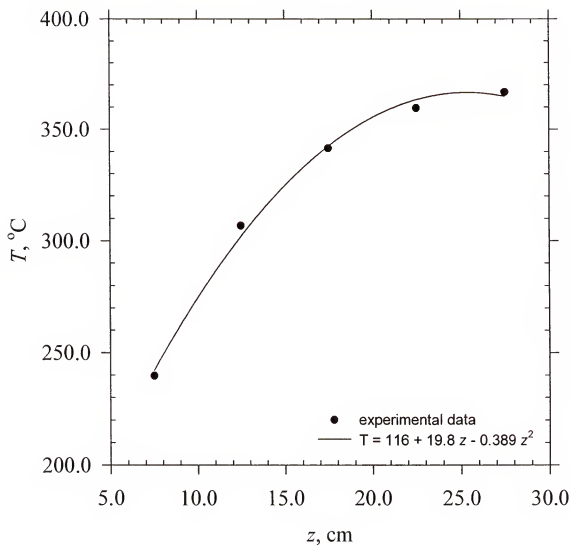


Figure 5-1. Temperature measurements (T) taken through the Zr chlorinator length (z). Argon was metered at $30 \text{ cm}^3 \text{ min}^{-1}$ through chlorinator at inlet ($z = 0.0$) $T = 25^\circ\text{C}$. The chlorinator length was 30 cm with OD:ID of 0.75:0.615 inches. The source temperature was held at 383°C .

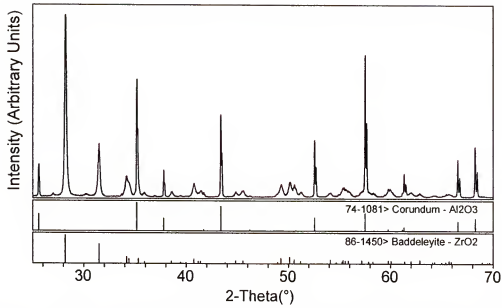


Figure 5-2. XRD result showing monoclinic zirconia (baddeleyite) and the corundum substrate. Deposition conditions given by run 4 in Table 5-2. Sample pattern is compared against known peak reflection for PDF cards for α -alumina (corundum) (middle, PDF card # 74-1081) and monoclinic zirconia (bottom, PDF card # 86-1450).

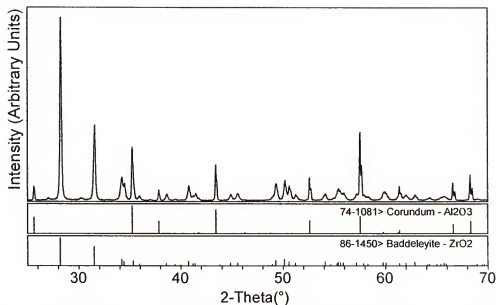


Figure 5-3. XRD result showing monoclinic zirconia (baddeleyite) and the corundum substrate. Deposition conditions given for run 5 in Table 5-2. Sample pattern is compared against known peak reflection for PDF cards for α -alumina (corundum) (middle, PDF card # 74-1081) and monoclinic zirconia (bottom, PDF card # 86-1450).

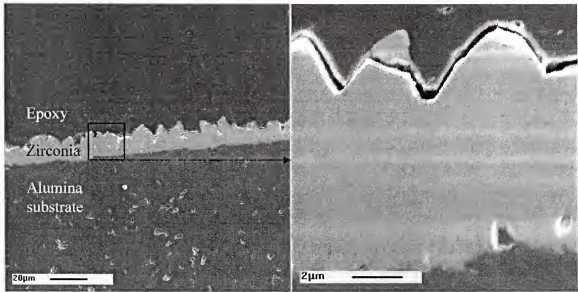


Figure 5-4. Electron micrographs of zirconia coating as deposited (run 5, Table 5-2). From left to right: Micrograph at 1000 $\times$ and 5000 $\times$.

CHAPTER 6

RESULTS AND DISCUSSION OF MOCVD USING BETA-DIKETONATES

This chapter presents and discusses the results on the MOCVD of YSZ coatings using β -diketonate precursors ($Y(tmhd)_3$ and $Zr(tmhd)_4$). A tetrahydrofuran (THF) solvent was used to prepare a metal-organic solution for liquid delivery. Details of the experimental conditions are given in Table 6-1.

6.1 Results

Low growth rates ($\sim 7 \mu\text{m h}^{-1}$) were obtained for coatings deposited with the base conditions given in Table 6-1 and the results of temperature investigation are given in Figure 6-1. Illustrated in Figure 6-1 is an Arrhenius plot of the growth rate as a function of temperature. The growth rate was estimated by weight gain (Eq. 4.10) and by SEM measurements. The average and standard deviation of the growth rate was determined by using the fracture cross-sections of selected sample coatings. The growth thickness was measured at 0.0, 0.5, 1.0, 1.5, and 2.0 cm points over the 2 cm sample diameter. Within each place-marker, 20 measurements were taken, from which the standard deviation was estimated. The electron micrographs of analyzed samples are given in (Figure 6-2 - Figure 6-5).

The surface-reaction limited and mass-transfer limited regimes of the growth data were easily observed (Figure 6-1). The surface-reaction limited regime was indicated by a relatively large dependence of the growth rate on temperature. This regime was found to exist over a wide temperature range (476–827°C) with an apparent activation energy

(E_a) of $59.9 \pm 5.67 \text{ kJ mol}^{-1}$. In addition, the mass-transfer limited regime was found above 827°C ($1000/T = 0.91$). This regime was indicated by a maximum deposition rate at 827°C with a slightly decreasing dependence of the growth rate on temperature above 827°C .

The efficiency was calculated by the ratio of the experimental growth rate to the thermochemical growth rate. The thermochemical calculations used the thermochemical conditions given in Table 6-1 (left-hand column) and assumed the following: (1) only tetragonal YSZ was allowed to form, (2) a 2 cm substrate was assumed for the surface area and (3) the calculations used a mol h^{-1} basis. The data used for the calculation were given in Chapter 3 and details on the conditions for calculation are given in Table 6-1. The calculation of the thermochemical growth rate was performed by first calculating the total mass of tetragonal YSZ deposited. Then Eq. (4.10) was used to determine the growth rate. The temperature was limited to a range from 750 – 1050°C since tetragonal YSZ forms within this temperature range with low yttrium content (Figure 3.4, $\text{YO}_{1.5}$ mole fraction < 0.1).

The efficiency of YSZ formation was low. This was evident by the comparison of experimental and thermochemical growth rates (Figure 6-6). For deposition at low temperature, the overall efficiency ($< 7\%$) was low at 745°C , then increased to $\sim 10\%$ at 827°C . Above 827°C , the efficiency dropped to $\sim 7\%$ (897°C).

Increasing the overall gas flow rate improved the maximum growth rate ($\sim 14 \mu\text{m h}^{-1}$). To study the effect of the overall gas flow rate, the overall gas flow was doubled by doubling the oxygen flow meter set point and doubling the syringe injection rate. The growth rate was plotted as a function of temperature (Figure 6-7) using SEM

cross-sectioned samples, which were analyzed for the average growth rate and standard deviation (as outlined above). The electron micrographs are seen in Figure 6-8 - Figure 6-11.

The surface-reaction limited and mass-transfer limited regimes of the growth data were easily observed (Figure 6-7). The surface-reaction limited regime was found to exist over a wide temperature range (476–827°C) with an apparent activation energy (E_a) of $50.85 \pm 4.327 \text{ kJ mol}^{-1}$. In addition, the mass-transfer limited regime was found above 827°C, with a similar slightly decreasing growth rate with increasing temperature above 827°C. In both sets of experiments (Figure 6-1 and Figure 6-7), it should be noted that increased chamber wall deposition was observed due to the formation of homogeneous nucleation for substrate temperatures above 827°C.

The microstructure of the coatings is seen in Figure 6-14. The electron micrograph showed that the YSZ coating was well adherent to the α -alumina substrate. The growth thickness was 10–11 μm in thickness and showed a layered microstructure.

The efficiency of YSZ formation was still low when comparing the experimental and thermochemical estimations of the growth rate (Figure 6-12). For deposition at low temperature, the overall efficiency (<7%) was low at 745°C, then increased to ~10% (827°C). Above 827°C, the efficiency dropped to ~7% (987°C).

The conformality of the coatings was determined by using SEM micrographs of the samples (Figure 6-2 to Figure 6-5 and Figure 6-8 to Figure 6-11) at five evenly spaced points over the 2 cm substrates. For example, the coating deposited at approximately 827°C (Figure 6-4) was measured for its thickness (Figure 6-13) over its cross-section. The coating conformality is thus defined as the average and standard

deviation of the coating thickness based on the measured growth thickness and experimental time (~50 minutes). The average and standard deviation for all coatings were then plotted (Figure 6-1 and Figure 6-7).

It was observed that the overall conformality of the coatings were within 10-15% of the average growth thickness. This was evident by the small standard deviation (Figure 6-1 and Figure 6-7, error bars) of SEM measurements over the sample cross-section. This suggested that the stagnation-plane flow injector provided for adequately uniform growth.

Results of x-ray diffraction analysis showed that the coatings were tetragonal in crystal structure with a preferred (1 0 1) orientation (Figure 6-15 - Figure 6-22). Figure 6-15 to Figure 6-18 are sample patterns for coatings deposited at the base conditions at four different temperatures and Figure 6-19 to Figure 6-22 were sample patterns for coatings deposited at twice the base overall flow rate at four different temperatures. For example, in Figure 6-17 (top), the sample pattern is given with both the coating and substrate. Below the sample pattern are the PDF cards that contain the peak reflections of powder diffracted samples of tetragonal YSZ (PDF card # 48-0224) and corundum (PDF card # 74-1001). The most distinct peak of tetragonal YSZ was seen at $30^\circ 2\theta$. Other peak reflections were seen for tetragonal YSZ at higher diffraction angles and their orientations are given in Appendix A. The tetragonal YSZ peaks, which are much more intense than the corundum peaks, indicate an appreciable coating thickness. The preferred orientation was indicated by the strong peak height at $30^\circ 2\theta$. The relatively low YSZ peak heights and high corundum peak heights are owed to smaller growth rate coatings at lower temperatures (Figure 6-15, Figure 6-16, Figure 6-19

, and Figure 6-20). The crystallite size was estimated by the Scherrer formula and was seen to increase with increasing temperature (Figure 6-23). This observation was typical of MOCVD processes (Soyez *et al.* 2000) and is attributed to a decreased density of nucleation centers with increasing growth temperature (Ashour 2003).

In YSZ MOCVD coatings, carbon co-deposition is undesirable. In these experiments, weight measurements before and after calcining indicated about 1-2% (by mass) of carbon had deposited. This carbon deposition could be on the coating surface as well as within the coating layers since the coatings turned from brownish-black or black to off-white after calcine.

6.2 Discussion

Successful deposition of single-phase, tetragonal YSZ was demonstrated. Using the aerosol-assisted liquid delivery (AALD) method, a maximum deposition rate of approximately $14 \mu\text{m h}^{-1}$ was obtained at a relatively moderate flow rate ($\sim 680 \text{ cm}^3 \text{ min}^{-1}$; assuming the liquid solution and oxygen were introduced as vapor at STP). Coating growth was seen to be rate limited by surface reactions below 827°C and rate limited by mass transfer above 827°C . The observed single-phase deposition suggests there was sufficient yttrium present to stabilize zirconia into the tetragonal phase.

Both the mass-transfer and surface-reaction limited regimes were within the established temperature ranges observed by others (as discussed in Chapter 2). In that discussion, the surface-reaction limited regime was seen to fall within a temperature range of $T < 740\text{--}770^\circ\text{C}$ (Kim *et al.* 2002). The mass-transfer limited regime was above $740\text{--}770^\circ\text{C}$ (Kim *et al.* 2002, Dubordieau *et al.* 1999), with a maximum growth rate observed between $770\text{--}840^\circ\text{C}$ (Jun *et al.* 2003, Dubourdieu *et al.* 1999, Kim *et al.* 2002).

In this work, the mass-transfer limited regime was marked by a maximum growth rate at 827°C and a slightly decreasing growth rate at higher temperatures (Figure 6-6 and Figure 6-12). Thus, confidence was given to the AALD method since the resulting growth data fell within the temperature bounds of both the surface-reaction and mass-transfer limited regimes reported by other authors (Pulver *et al.* 2000, Kim *et al.* 2002, Dubordieau *et al.* 1999).

The observed growth rate decrease above 827°C indicated that precursor depletion in the gas phase occurred above the substrate. According to Pulver *et al.* (2000), this precursor depletion was due to homogeneous nucleation of YSZ. The increased precursor depletion occurred because of the increased substrate heating (Pulver *et al.* (2000)). As the susceptor was heated to higher temperatures (to heat the substrate above 827°C), the radiative heat transfer from the susceptor to the gas phase increased. This increased radiative heat transfer caused the gas stream to have a higher temperature above the substrate, thus causing the pre-reaction of the precursors in the gas phase to cause homogeneous nucleation (Pulver *et al.* 2000).

The growth in the surface reaction limited regime had a lower overall thermal activation barrier as opposed to past researchers (Table 2.2). On one hand, the activation energies (50.9 and 59.9 kJ mol⁻¹) reported here were obtained using the AALD method. On the other hand, Pulver *et al.* (2000), Kim *et al.* (2002), and Dubordieau *et al.* (1999) reported activation energies between 104–160 kJ mol⁻¹. These workers used a combined sublimation and inert carrier gas method for precursor transport to the substrate (Pulver *et al.* 200, Kim *et al.* 2002, and Dubordieau *et al.* 1999). The only differences between past researchers and this work were the use of a solvent for the AALD method in this work.

According to Chiang *et al.* (1992), the solvent was responsible for improving gas-phase precursor transport to the substrate (Chiang *et al.* 1992, Hubert-Pfalzgraf). Essentially, the solvent forms a complex with the solid precursor (Hubert-Pfalzgraf). Consequently, the vapor pressure of this solvent-precursor complex is higher than the precursor vapor pressure alone (Chiang *et al.* 1992, Hubert-Pfalzgraf). When the solution is heated, the solvent-precursor complex vaporizes at lower temperatures without any decomposition or decomplexation (Chiang *et al.* 1992). The solvent-precursor complex introduction into the gas phase was further enhanced in this work by the use of an ultrasonic atomizer, which misted fine droplets of the precursor for rapid volatilization at 300°C (Wang *et al.* 2000, Matsuzaki *et al.* 1999).

This improved gas-phase transport was evident when comparing the growth rates and activation energy of this work and that of Garcia *et al.* (1997). In their experiments, a high Y(tmhd)₃ and Zr(tmhd)₄ gas phase mole fraction (> 0.1) was achieved by sublimation and inert carrier gas transport (overall flow rate of approximately 600) (Garcia *et al.* 1997). The growth rates obtained by Garcia *et al.* (1992), however, did not exceed 1.1 μm h⁻¹. The close agreement of the activation energies between this work and Garcia *et al.* (1992) suggests that the mechanism was not altered by the solvent, just that the transport of the precursor was improved (Garcia *et al.* 1992). This improved precursor transport is indicated by the relatively high growth rate (~ 14 μm h⁻¹) of this work as compared to the maximum growth rate (~ 1.1 μm h⁻¹) obtained by Garcia *et al.* (1992).

The similarities in activation energy suggests that the solvent did not play a role in the growth process of YSZ. Chiang *et al.* (1992) suggested that prior to arrival on the

surface, the solvent decomplexes from the precursor. This was evident when mass spectrometric studies revealed that the same precursor decomposition pathway occurred with or without the use of a solvent (Chiang *et al.* 1992). This meant that the decomposition mechanism for the growth of YSZ on the substrate surface only followed the pathway of precursor adsorption, surface reaction, and reaction by-product desorption (Chiang *et al.* 1992, Pulver *et al.* 2000, Igumenov *et al.* (2001).

The formation of carbon may be owed to the precursor ligand or solvent. Such carbon formation may involve the adsorption and incomplete decomposition and/or desorption of the precursor ligand or solvent on the surface (Igumenov *et al.* 2001, Chiang *et al.* 1992, Turgambeava *et al.* 1997). Such incomplete decomposition was probably owed to low system oxygen (Igumenov *et al.* 2001). This low system oxygen was confirmed thermochemically when carbon formation was predicted for low oxygen environments (Figure 3.33, $n_O / (n_Y + n_{Zr}) = 350$). If there was low system oxygen, the formation of volatile CO₂ and CO was inhibited (Figure 3.34, $n_O / (n_Y + n_{Zr}) = 350$), thus disallowing the desorption of carbon from the surface and trapping of carbon within or on top of the coating layers (Igumenov *et al.* 2001).

In comparing the experimental and thermochemical growth rates, it was seen that the efficiency for the MOCVD processes was low (Figure 6-6 and Figure 6-12). The low efficiency was not dependent on reaction chamber geometry due to the use of a stagnation-plane flow injector (as discussed in Chapter 4). The low efficiency could be due to the high susceptor temperature causing gas flow recirculation above the substrate. As discussed in Chapter 4, the high substrate temperature relative to the inlet gas temperature and low inlet flow rate can contribute to recirculation of the gas flow. This

recirculation is reflected in a high Gr/Re^2 ratio. In this work, the substrate-inlet distance (1 cm), the gas velocity (2.3 cm s^{-1}), the substrate temperature (827°C), and the gas inlet temperature (200°C) are known and can be used with Eq. (4.12) to calculate a Gr/Re^2 (225). This high Gr/Re^2 ratio suggests the possible “rolling” of the gas flow as it impinges onto the hot substrate. This rolling of the gas flow in the immediate substrate region can cause recirculation, which forces reagents to be swept away from the substrate and can react or re-condense further downstream. In this work, the evidence of reactor wall deposition downstream of the reaction zone suggests that some of the unreacted gas passes by the substrate and reacts further downstream. Although the efficiency of deposition was low when comparing the experimental and thermochemical growth rates, the efficiency in this work was as high as 10%, which can be considered relatively high as compared to most MOCVD processes (Pierson 1992).

Further, the thermochemical growth rate never decreased with increasing temperature, whereas experimentally, this did occur. This decrease in growth rate with increasing temperature was due to the depletion of the precursor in the gas phase (as discussed above). Such depletion would not be predicted thermochemically since homogeneous nucleation could not be incorporated in the calculation.

The MOCVD process had many differences as compared to the chloride CVD process. First, lower deposition temperatures were feasible for MOCVD. This was evident by the growth of YSZ layers in MOCVD at temperature for which chloride precursors cannot achieve the same deposition rates.

Second, the Y- and Zr- β -diketonate precursors were more effective for CVD than their Y- and Zr-chloride counterparts. The Y- and Zr- β -diketonate precursors had a

higher volatility than Y- and Zr-chloride precursors. Further, the introduction of the Y- and Zr- β -diketonate precursors to the reactor was enhanced by the use of a solvent and the AALD method (as discussed above).

Finally, the activation energies observed in this work were lower than the activation energies reported in the chloride CVD literature. In chloride CVD using the RWGSR, reaction with the metal chlorides was limited by surface water formation (Minet *et al.* 1987, Brennfleck *et al.* 1981). In this chapter, however, it was observed that the activation energy was much lower than in chloride CVD. This low activation energy suggests that the mechanism of precursor adsorption, surface reaction, and reaction by-product desorption in MOCVD processes had a lower overall thermal activation barrier than the RWGSR mechanism of surface water formation. These lower thermal activation energies exhibited by MOCVD were compounded with the benefit of lower temperature to overcome this thermal activation barrier for moderate growth rate coatings.

Table 6-1. Thermodynamic and Experimental Conditions for Deposition of YSZ.

Thermochemical Condition or Variable	Value	Experimental Condition or Variable	Value
Temperature	800-1000 (°C)	Substrate Temperature	475-987 (°C)
Pressure	1013.25 Pa	Reactor Pressure	1013.25 Pa
$n_{Zr} + n_Y$	0.000441, 0.000882 mol min ⁻¹	Syringe delivery rate *	0.875, 1.75 ml min ⁻¹
$n_C = 1044n_{Zr} + 1033n_Y$	0.46, 0.92 mol min ⁻¹	Precursor Solution Data	Y(C ₁₁ H ₁₉ O ₂) ₃ : Zr(C ₁₁ H ₁₉ O ₂) ₄ By Mass 1:7
$n_H = 2076n_{Zr} + 2057n_Y$	0.91, 1.82 mol min ⁻¹		Total Mass 4 g
$n_O / (n_Y + n_{Zr})$	300		THF (C ₄ H ₈ O) Volume 100 ml
$n_Y / (n_Y + n_{Zr})$	0.08		Precursor Solution Molarity 0.0083 M Y 0.0421 M Zr
$n_{O,min} = 258n_{Zr} + 256n_Y$	0.11, 0.22 mol min ⁻¹	Oxygen Flow Rate *	100, 200 sccm

* Base conditions given first, then 2x base condition given. (e.g. the syringe delivery rate was 0.875 ml min⁻¹ then was doubled to 1.75 ml min⁻¹ for deposition at 2x base overall flow rate)

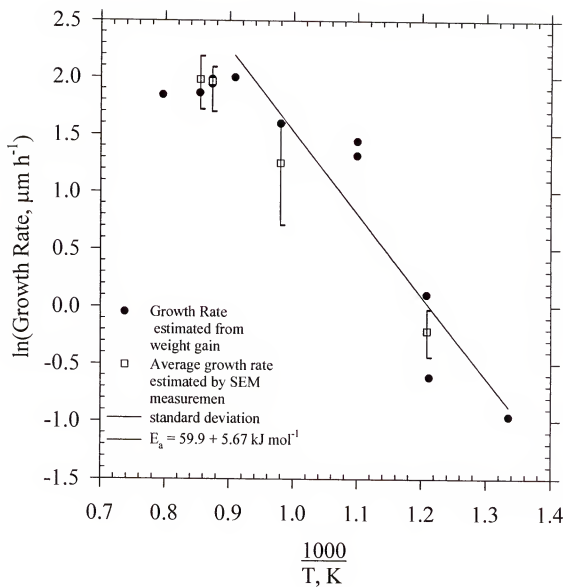


Figure 6-1. Arrhenius plot of experimental data using base conditions (Table 6-1). Surface reaction limited regime indicated by growth temperatures less than 827°C ($1000/T > 0.9$). Mass-transfer limited regime indicated by no line for growth temperatures greater than 827°C ($1000/T < 0.9$).

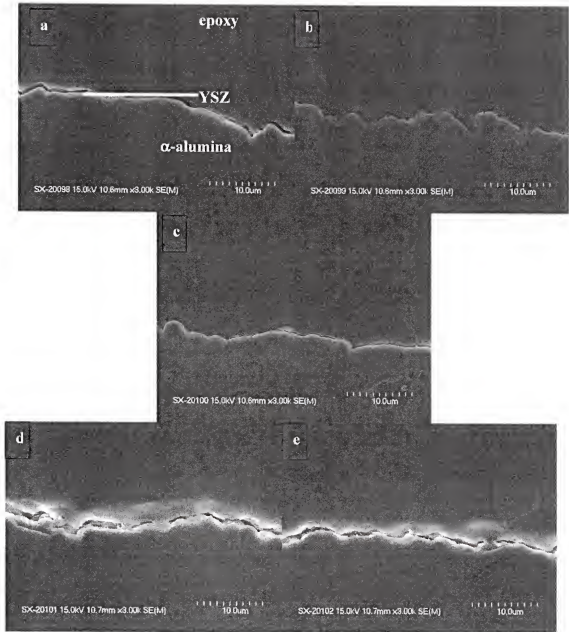


Figure 6-2. Electron micrographs of fracture cross-sectioned sample at a) 0, b) 0.5, c) 1.0, d) 1.5, and e) 2.0 cm over the 2 cm sample diameter (from left to right, top to bottom). Sample fabricated at 550°C and the base overall flow rate.

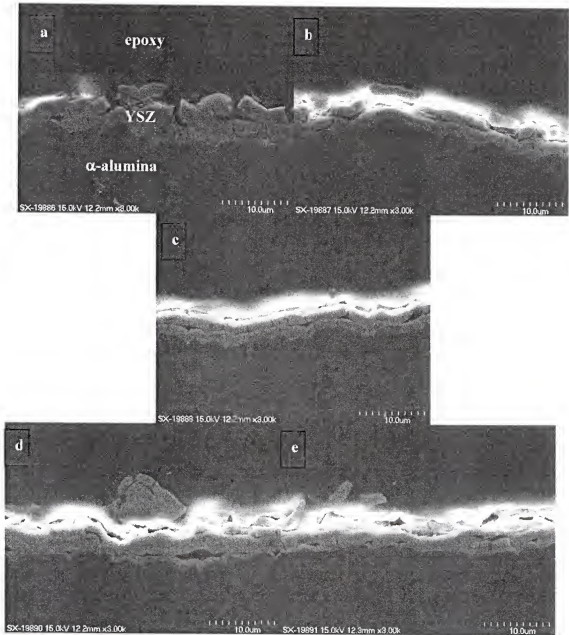


Figure 6-3. Electron micrographs of fracture cross-sectioned sample at a) 0, b) 0.5, c) 1.0, d) 1.5, and e) 2.0 cm over the 2 cm sample diameter (from left to right, top to bottom). Sample fabricated at 745°C and the base overall flow rate.

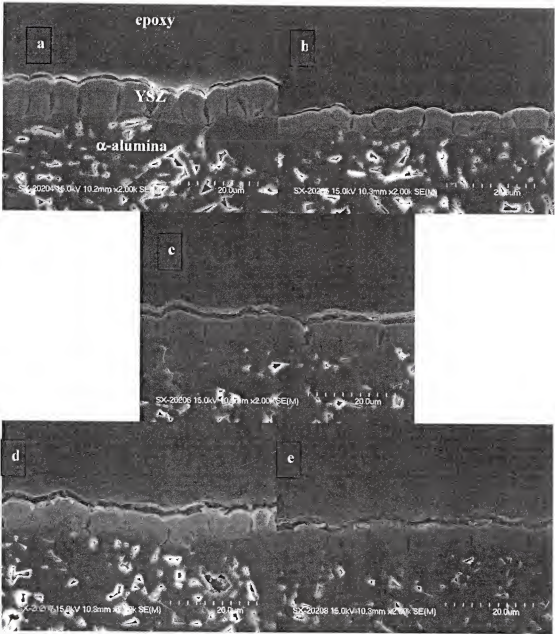


Figure 6-4. Electron micrographs of fracture cross-sectioned sample at a) 0, b) 0.5, c) 1.0, d) 1.5, and e) 2.0 cm over the 2 cm sample diameter (from left to right, top to bottom). Sample fabricated at 827°C and the base overall flow rate.

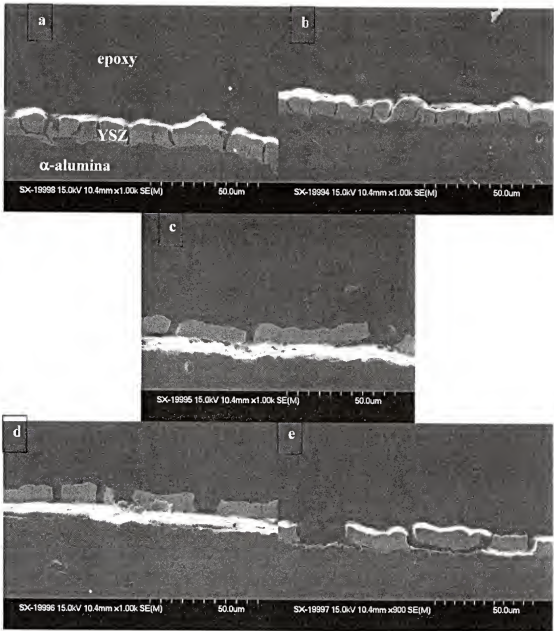


Figure 6-5. Electron micrographs of fracture cross-sectioned sample at a) 0, b) 0.5, c) 1.0, d) 1.5, and e) 2.0 cm over the 2 cm sample diameter (from left to right, top to bottom). Sample fabricated at 897°C and the base overall flow rate.

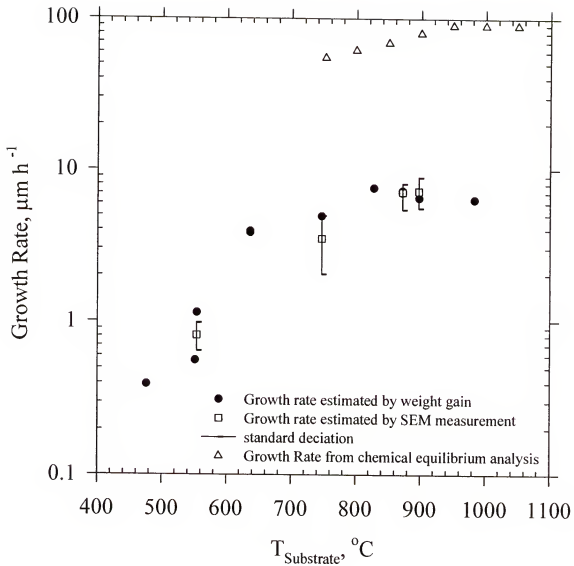


Figure 6-6. Plot of growth rate estimated by weight gain, SEM measurement (for quality assurance), and thermochemical calculations. Experimental and thermochemical conditions given in Table 6-1 for base reagent overall flow rate.

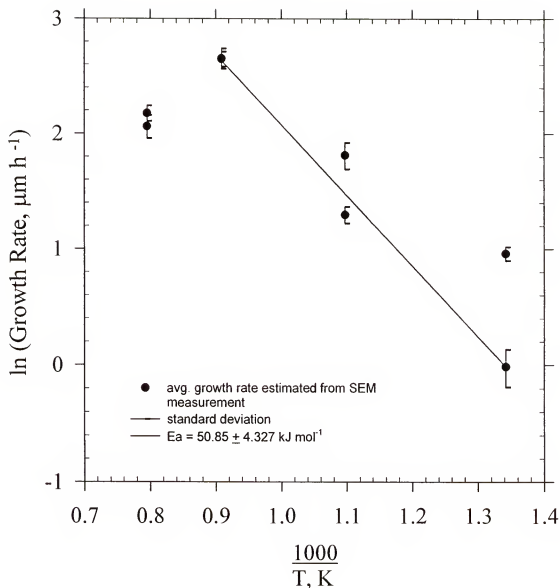


Figure 6-7. Arrhenius Arrhenius plot of experimental data using $2\times$ base overall flow rate. Surface reaction limited regime indicated by growth temperatures less than 827°C ($1000/T > 0.9$). Mass-transfer limited regime indicated by no line for growth temperatures greater than 827°C ($1000/T < 0.9$).

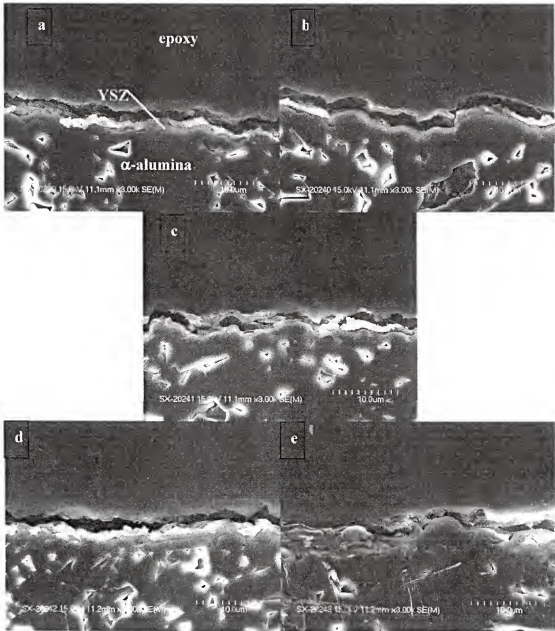


Figure 6-8. Electron micrographs of fracture cross-sectioned sample at a) 0, b) 0.5, c) 1.0, d) 1.5, and e) 2.0 cm over the 2 cm sample diameter (from left to right, top to bottom). Sample fabricated at 476°C and twice the base overall flow rate.

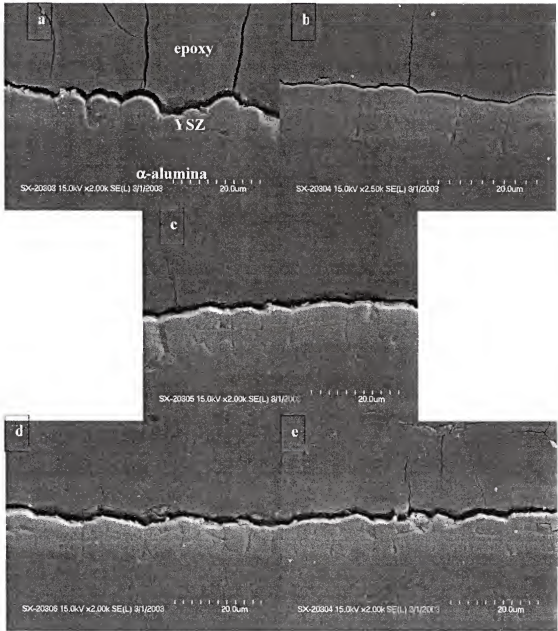


Figure 6-9. Electron micrographs of fracture cross-sectioned sample at a) 0, b) 0.5, c) 1.0, d) 1.5, and e) 2.0 cm over the 2 cm sample diameter (from left to right, top to bottom). Sample fabricated at 636°C and twice the base overall flow rate.

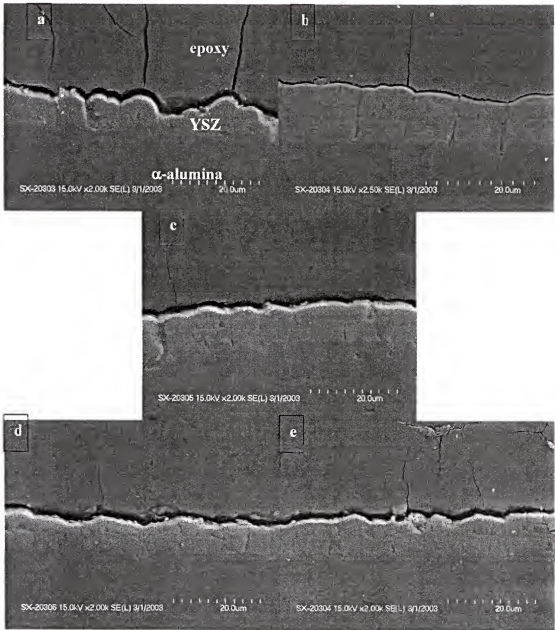


Figure 6-10. Electron micrographs of fracture cross-sectioned sample at a) 0, b) 0.5, c) 1.0, d) 1.5, and e) 2.0 cm over the 2 cm sample diameter (from left to right, top to bottom). Sample fabricated at 827°C and twice the base overall flow rate.

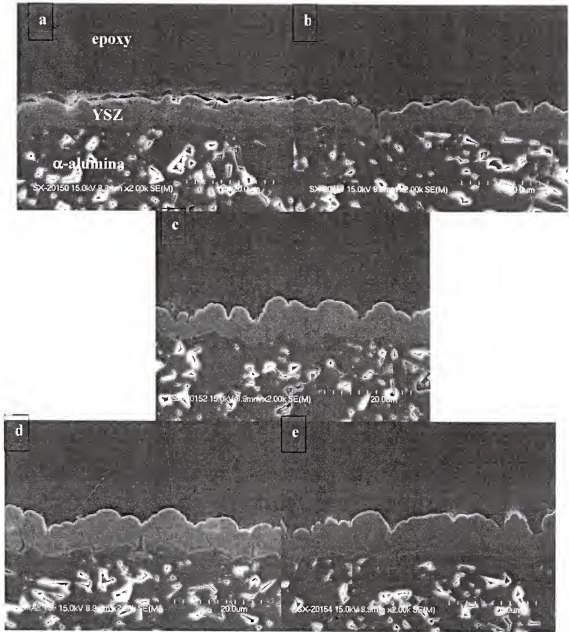


Figure 6-11. Electron micrographs of fracture cross-sectioned sample at a) 0, b) 0.5, c) 1.0, d) 1.5, and e) 2.0 cm over the 2 cm sample diameter (from left to right, top to bottom). Sample fabricated at 987°C and twice the base overall flow rate.

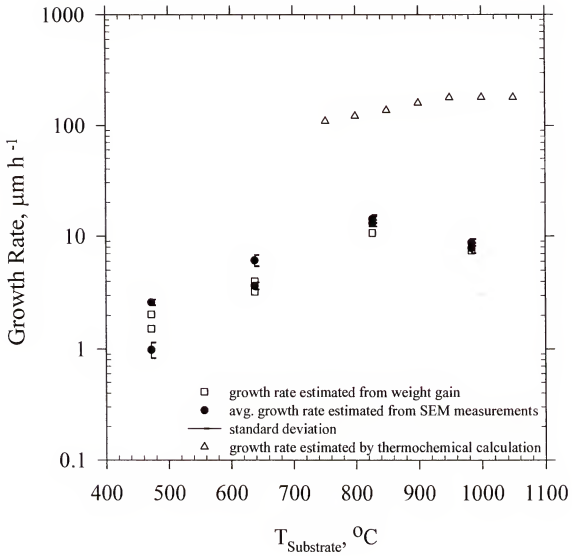


Figure 6-12. Plot of growth rate estimated by weight gain, SEM measurement (for quality assurance), and thermochemical calculations. Experimental and thermochemical conditions given in Table 6-1 for 2x base overall flow rate.

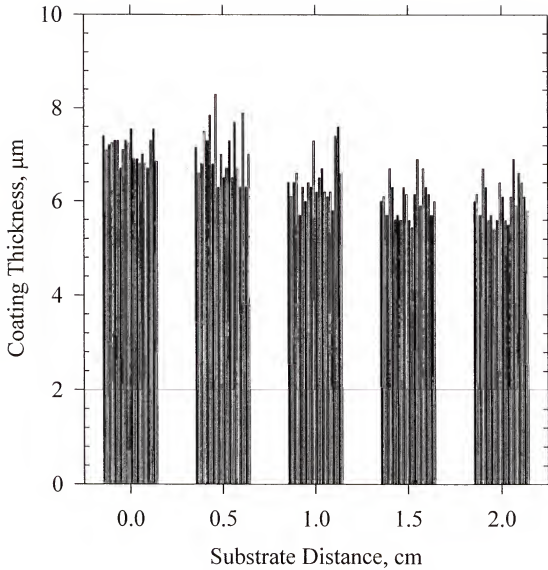


Figure 6-13. Plot of coating thickness over the coating cross-section. The substrate distance represents the point over the substrate cross-section. Distances 0.0 to 2.0 correspond to micrographs a to e, respectively, in Figure 6-4. The points labeled 0.0 and 2.0 are the substrate edge and 1.0 is the substrate center.

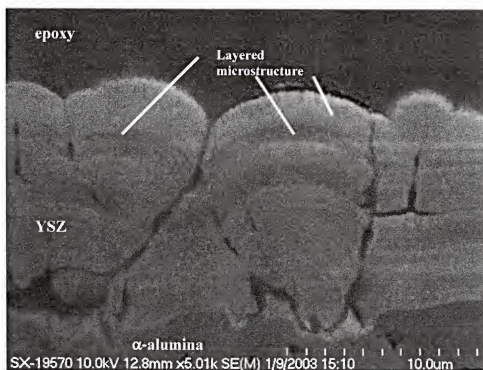


Figure 6-14. Electron micrograph of YSZ coating. Notice the coating has a layered microstructure as they begin to grow in the columnar direction. The deposition conditions were the same as those for Figure 6-10 for a 45 minute experiment.

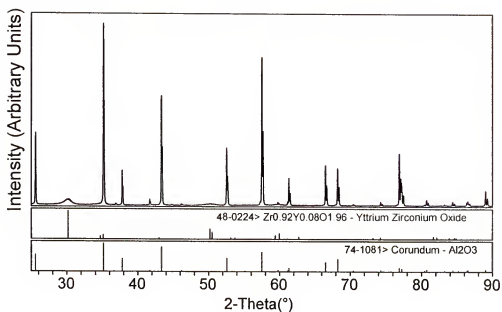


Figure 6-15. XRD pattern for growth at 550°C and base overall flow rate. Sample pattern is compared against known peak reflections for tetragonal YSZ (PDF card # 48-0224) and α -alumina (corundum) (PDF card # 74-1081).

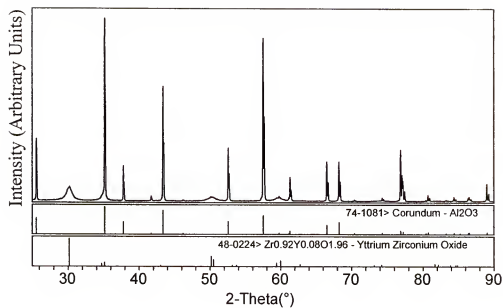


Figure 6-16. XRD pattern for growth at 745°C and base overall flow rate. Sample pattern is compared against known peak reflections for α -alumina (corundum) (PDF card # 74-1081) and tetragonal YSZ (PDF card # 48-0224).

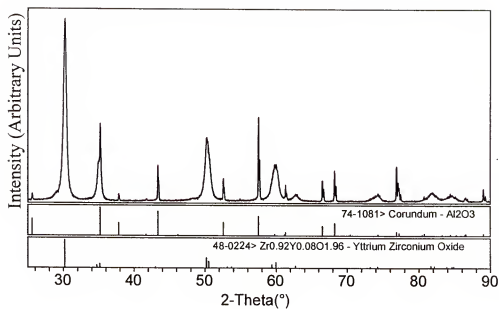


Figure 6-17. XRD pattern for growth at 827°C and base overall flow rate. Sample pattern is compared against known peak reflections for α -alumina (corundum) (PDF card # 74-1081) and tetragonal YSZ (PDF card # 48-0224).

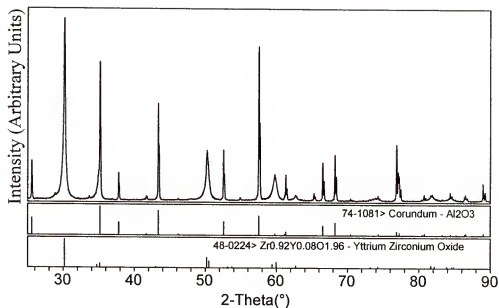


Figure 6-18. XRD pattern for growth at 897°C and base overall flow rate. Sample pattern is compared against known peak reflections for α -alumina (corundum) (PDF card # 74-1081) and tetragonal YSZ (PDF card # 48-0224).

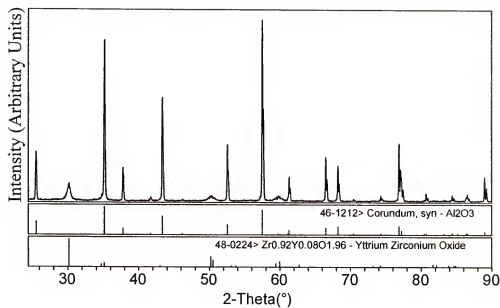


Figure 6-19. XRD pattern for growth at 476°C and 2×base overall flow rate. Sample pattern is compared against known peak reflections for α -alumina (corundum) (PDF card # 46-1212) and tetragonal YSZ (PDF card # 48-0224).

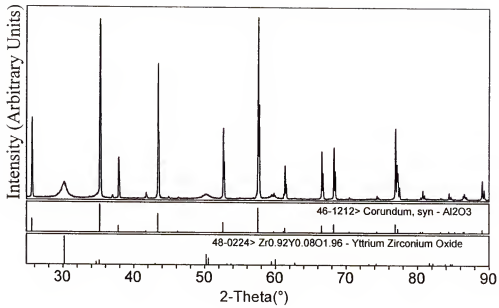


Figure 6-20. XRD pattern for growth at 636°C and 2×base overall flow rate. Sample pattern is compared against known peak reflections for α -alumina (corundum) (PDF card # 46-1212) and tetragonal YSZ (PDF card # 48-0224).

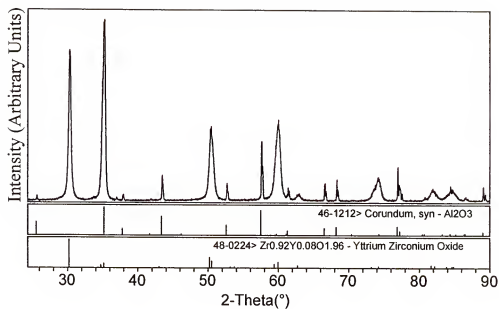


Figure 6-21. XRD pattern for growth at 827°C and 2×base overall flow rate. Sample pattern is compared against known peak reflections for α -alumina (corundum) (PDF card # 46-1212) and tetragonal YSZ (PDF card # 48-0224).

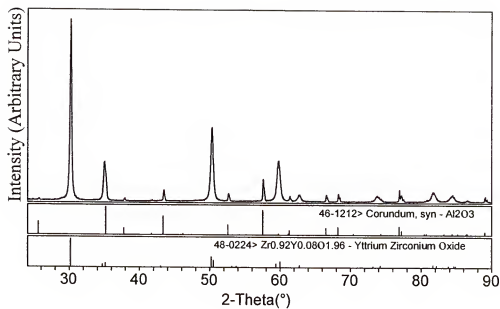


Figure 6-22. XRD pattern for growth at 987°C and 2×base overall flow rate. Sample pattern is compared against known peak reflections for α -alumina (corundum) (PDF card # 46-1212) and tetragonal YSZ (PDF card # 48-0224).

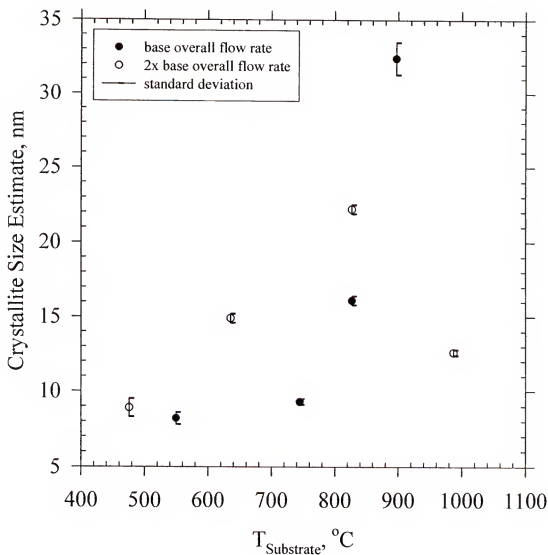


Figure 6-23. Plot of crystallite size estimate for tetragonal YSZ coatings as a function of substrate temperature. Crystallite size estimated by Scherrer formula using tetragonal peak at $30^\circ 2\theta$ (in sample pattern of Figure 6-15 to Figure 6-22) and PDF card # 48-0224.

CHAPTER 7

RESULTS AND DISCUSSION OF MOCVD USING N-BUTOXIDES

This chapter presents and discusses the results of MOCVD experiments using $\text{Y}(\text{OBut}^n)_3$ and $\text{Zr}(\text{OBut}^n)_4$. The solvents used were toluene and *n*-butanol, respectively. The conditions are given in Table 7-1. Please note that a number of experimental results were discarded due to the lack of reproducibility while using this precursor solution with the stagnation-plane flow injector. The lack of reliability in the collected growth rate data was due to clogging within the stagnation-plane flow injector. This clogging was associated with precursor pre-reaction within the injector. Thus, the stagnation plane flow injector was removed, and the growth was performed in an axisymmetric gas flow profile.

7.1 Results

High growth rate ($\sim 43 \mu\text{m h}^{-1}$) coatings were achieved at 1005°C . This high growth rate was achieved in the mass-transfer limited regime. Both the mass-transfer limited and the surface-reaction limited regimes were determined by studying the influence of the growth temperature on the growth rate (Figure 7-1 and Figure 7-2). In both figures, an Arrhenius dependence of the growth rate was observed between 845 and 960°C . Apparent activation energies were reported for both weight gain estimated (Figure 7-1) and SEM measured (Figure 7-2) growth rates of the same samples. The SEM measurements were similar to those described in Chapter 6. It can be seen that

there was very good agreement between both estimates of the growth rate and activation energy.

The conformality of the coatings was determined by using SEM micrographs of the samples (Figure 7-3 to Figure 7-8) at five evenly spaced points over the 2 cm substrates. For example, the coating deposited at 1005°C (Figure 7-8) was measured for its thickness (Figure 7-9) over its cross-section. The coating conformality is thus defined as the average and standard deviation of the coating thickness based on the measured growth thickness and experimental time (~80 minutes). The average and standard deviation for all coatings were then plotted (Figure 7-2).

It was observed that the overall conformality of the coatings were within 15-20% of the average growth thickness. This was evident by the small standard deviation (Figure 7-2, error bars) of SEM measurements over the sample cross-section. This suggested that the axisymmetric gas flow provided for adequately uniform and high growth rate coatings.

Using the Y- and Zr-*n*-butoxide precursors slightly improved the overall efficiency of the deposition process as compared to Y- and Zr- β -diketonate precursors (Figure 7-10). In Figure 7-10, the raw growth rate data and SEM measurements were compared to the thermochemical growth rate data (calculation described in Chapter 6 with thermochemical conditions given in Table 7-1). It was seen that the efficiency (~5.5%) at lower temperatures (< 845°C) was lower than the efficiency (~12.5%) at higher temperatures (> 1000°C). The increase in efficiency with increasing temperature reflects the kinetic hindrance of the growth rate at lower temperatures.

SEM micrographs of samples are shown in Figure 7-3 through Figure 7-8. These micrographs represent the measured growth rates given in Figure 7-2. It is seen that the growth was columnar in microstructure, which is necessary for strain-tolerance during thermal cycling. A layered, or “banded”, type growth was also seen within the columnar grains.

Although the coating growth rate, coating conformality, and coating microstructure were desirable, the results of characterization studies showed that the formation of secondary phases was possible. X-ray diffraction studies showed the presence of a mixture of both tetragonal and monoclinic crystal structures (Figure 7-11). Using the JADE computer software package, the monoclinic crystal structure was seen to have a $(-1\ 1\ 1)$ (at $28^\circ\ 2\theta$) and $(1\ 1\ 1)$ (at $31.5^\circ\ 2\theta$) preferred orientation and the tetragonal crystal structure was seen to have the desired $(1\ 0\ 1)$ (at $30^\circ\ 2\theta$) preferred orientation (Figure 7-11).

Since secondary-phase formation was evident, it was necessary to quantify the relative amount of each phase that formed. The relative amount of tetragonal phase was given in Table 7.2 with the monoclinic phase making up the balance of the two-phase mixture. The relative amount of tetragonal phase was determined by comparing the relative peak heights of both the monoclinic and tetragonal peak heights as they compared to their corresponding PDF cards (the reference intensity ratio, Chapter 4). The coating samples had a low tetragonal character, which was not a beneficial aspect to the deposition process.

The crystallite size of the tetragonal phase was seen to increase as temperature increased for the tetragonal phase (up to 845°C , Table 7-2). Above 845°C , the crystallite

size was seen to decrease with increasing temperature. The increase in crystallite size was estimated using the Scherrer formula. The increased crystallite size with increasing growth temperature was typical in MOCVD (Soyez *et al.* 2000). The decrease in crystallite size, however, unusual and is attributed to the decreasing tetragonal character of the coating with increasing temperature. The low peak intensity at $30^\circ 2\theta$ for increasing growth temperature suggests that more nucleation centers appear in the tetragonal phase of the coatings

The formation of the monoclinic phase was owed to the low yttrium presence within the coating. The evidence of low yttrium content was confirmed using compositional analysis (EPMA) of the coatings (Figure 7-12 to Figure 7-17). On the vertical axis is the coating thickness (where the YSZ-metallic interface is at 0 μm) and on the horizontal axis is increasing yttrium content ($n_Y / (n_Y + n_{Zr}) \times 100\%$). To obtain the result shown in these figures, the relative atomic compositions of oxygen, yttrium, and zirconium were first tabulated through the coating thickness. Since the oxygen content was found to be stoichiometric, it was only necessary to report the $n_Y / (n_Y + n_{Zr})$ ratio. This ratio could then be compared to the $n_Y / (n_Y + n_{Zr})$ ratio (~ 0.08) in the precursor solution.

The reason for the monoclinic phase appearing in the coatings can be explained by comparing the EPMA results with the phase diagram (Figure 3-4). It can be seen that the low yttrium content presented by the EPMA results correspond to the formation of monoclinic zirconia. For example, the coating deposited at 845°C , the coating had an average $n_Y / (n_Y + n_{Zr})$ ratio of 0.021. According to Figure 3.4, the phases formed at this

$n_Y / (n_Y + n_{Zr})$ ratio are a mixture of predominantly monoclinic phase and a lesser amount of tetragonal YSZ.

The results showed that the fraction of yttrium in the coating relative to zirconium was low at lower growth temperatures and, in general, increased as temperature increased. Approximately 25% of the yttrium in the solution $(n_Y / (n_Y + n_{Zr}) \times 100\% = 8\%)$ was incorporated in the film. This percentage increased to as high as 45%, at higher deposition temperatures (1005°C). Despite the increase in yttrium content with increasing temperature, the monoclinic phase of YSZ still dominated the two-phase coating mixture that formed.

Finally, carbon co-deposition was apparent. This carbon appeared on the surface (and possibly within the coating) as a charcoal-colored layer (Burleson 2002, Cameron and George 2001). When the coatings were calcined for 4 hours at 1000°C, the coatings had an off-white color and lost weight (Figure 7-18). This weight change is associated with the “burning-off” of any carbon from the coating. It was not feasible to perform EPMA analysis for carbon due to the sample being mounted in an epoxy resin.

7,2 Discussion

The successful growth of high deposition rate coatings was obtained using Y- and Zr-*n*-butoxide precursors with the AALD method. The coating growth was limited by surface reactions below 960°C, and limited by mass transfer above 960°C. The kinetic hindrance at lower growth temperatures caused the low overall efficiency (precursor utilization) and growth rates as compared to the higher precursor utilization at higher growth temperatures.

The large gap between the experimental and thermochemical growth rates (Figure 7-10) meant that the overall efficiency of the deposition process was low. In this work, the efficiency is defined as the ratio of the experimental growth rate to the thermochemical growth rate. The thermochemical analysis assumed that all of the gas flow reaches the 2 cm substrate (i.e. the substrate surface area and the chamber wall inner cross-sectional area are equal), thus obtaining a high growth rate (e.g. $350 \mu\text{m h}^{-1}$ at 1005°C in Figure 7-10). The low efficiency can be explained by the effect of the reactor chamber geometry (as explained in Chapters 4). In axisymmetric flow, the amount of gas flow that reaches the substrate is dependent on the surface area of the substrate relative to the inner cross-sectional diameter of the reactor chamber wall. The substrate diameter was 2 cm and the chamber wall was 4.6 cm. This means that the substrate surface area is approximately 16% of the inner cross-sectional area of the chamber wall. This means that only 16% of the gas flow reaches the substrate surface.

Thus, if the substrate diameter is increased or if multiple samples are used, then the efficiency of growth could increase. For example, if the substrate diameter is increased by a factor of two, the surface area would be increased by a factor of 4. This would increase the amount of precursors that reach the substrate surface. Consequently, the growth efficiency could be improved to nearly 50%, which is extremely high for CVD processes (Tu et al. 2002).

The activation energies ($E_a = 53.81$ and $63.06 \text{ kJ mol}^{-1}$) obtained in this work agreed favorably with the activation energies obtained by Garcia *et al.* (1997) and Chour *et al.* (1997). Garcia *et al.* (1997) and Chour *et al.* (1997) both obtained low activation energies ($E_a = 58$ and 45.5 kJ mol^{-1} , respectively) in their CVD experiments. Further,

Garcia *et al.* (1997) and Chour *et al.* (1997) did not utilize a solvent for precursor delivery while using $\text{Y}(\text{tmhd})_3$ and $\text{Zr}(\text{tmhd})_4$ and $\text{Y}(\text{tmhd})_3$ and $\text{Zr}(\text{OBut}^n)_4$, respectively. The close agreement of these activation energies suggests that the solvent did not play a role in the growth mechanism of YSZ.

The growth temperatures in this work, however, were higher than that of Chour *et al.* (1997). In this work, the surface-reaction limited regime was found at high temperature (845–960°C) for the formation of YSZ using $\text{Y}(\text{OBut}^n)_3$ and $\text{Zr}(\text{OBut}^n)_4$ and flowing O_2 . Chour *et al.* (1997) used water vapor with flowing oxygen gas as an oxygen source. When this oxygen source reacted with $\text{Y}(\text{tmhd})_3$ and $\text{Zr}(\text{OBut}^n)_4$, cubic YSZ formation was surface-reaction limited at lower temperatures (< 837°C) (Chour *et al.* 1997). The addition of water vapor to the flowing O_2 gas suggested that water vapor lowered the temperature range for surface-reaction limited growth. This lowering of the surface-reaction limited temperature range may be due to the formation of the same surface reaction intermediates at lower temperatures (Igumenov *et al.* 2001).

In comparison with MOCVD using β -diketonate precursors, it was apparent that the increased growth rates were simply owed to the increased gas phase concentration of the *n*-butoxide precursors. This relatively high gas phase concentration ($x_Y + x_{Zr} = 0.0015$ for *n*-butoxide precursors as compared to $x_Y + x_{Zr} = 0.00003$ for β -diketonate precursors), in turn, was owed to the relatively high precursor solution concentration, (Lane *et al.* 1998). This meant that in the mass-transfer limited regime, the growth rate increased with increased precursor solution concentration.

Yet, in the surface-reaction limited regime, the higher growth rate is not explained by the higher precursor flux to the substrate. Rather, the higher growth rates in the

surface-reaction limited regime may be due to the formation of different surface-reaction intermediates during the surface decomposition of metal-*n*-butoxide precursors as compared to the surface decomposition of the metal- β -diketonate precursor decomposition. A mechanism is not proposed here, however, this can be determined using mass-spectrometry/gas chromatography *in situ* during the growth of YSZ using metal- β -diketonate and metal-*n*-butoxide precursors.

The thermochemical study (Chapter 3, Zr-Y-O-C-H system) predicted no carbon formation (for deposition using the conditions in Table 7-1), however, carbon was seen on the coating surface and, perhaps, was within the coating layers. This carbon was “burned-off” after calcining at 100°C for 4 hours. The amount of carbon that formed during growth and burned-off during calcining was shown in Figure 7-18, and was seen to decrease with increasing temperature. According to Burleson *et al.* (2002) and Cameron and George (1999), who observed carbon formation using $\text{Zr}(\text{O}i\text{Bu})_4$ to deposit ZrO_2 , the carbon formation was attributed to the precursor ligand. Based on mass-spectrometric results, they found that carbon formation was due to the decreased desorption of carbon from the surface as CO or CO₂. Cameron and George suggested that a competing mechanism occurred such that incomplete decomposition/desorption of the precursor ligand occurred and carbon was trapped on the surface. The decrease of carbon formation with increasing temperature could be attributed to the increased desorption of carbon by reaction with the available oxygen at high temperature to form volatile CO and CO₂.

Since some carbon still formed at the higher temperatures (1005°C and 1012°C), it was possible that the decomposition of the solvent and/or precursor ligand may have

led to such carbon formation. In order to determine the principle source of this carbon, mass-spectrometry and gas-chromatography should be performed *in situ* with the precursor and solvent in separate studies. According to Chiang *et al.* (1992), Igumenov *et al.* (2001), and Chour *et al.* (1997), further removal of solid carbon may be accomplished by adding water vapor to the flowing oxygen gas.

Finally, the low yttrium content was not beneficial to the deposition of tetragonal YSZ. The low yttrium content allowed for phase transformation after the coatings underwent one thermal cycle (calcined in lab air at 1000°C and then brought back to room temperature). The cause of this low yttrium content was not found. It was possible that $\text{Y}(\text{OBut}^n)_3$ may have undergone pre-reaction in the gas phase (there was significant chamber wall deposition).

It is also possible that the $\text{Y}(\text{OBut}^n)_3$ may have been difficult to decompose in the gas phase due to the possible oligimerization of this precursor. (Bradley 1989) Oligimerization is the formation of “branched” metal-organic structures in which the metal center from one metal-organic molecule bonds to the ligand of another metal-organic molecule. The resulting complex that forms is more resistant to thermal decomposition. (Bradley 1989)

Table 7-1. Experimental and Thermochemical Matrix For Deposition of YSZ

Thermodynamic Condition or Variable	Value	Experimental Condition or Variable	Value
Temperature	800–1050°C	Substrate Temperature	450–1012 °C
Pressure	1013.25 Pa	Reactor Pressure	1013.25 Pa
$n_{Zr} + n_Y$	0.0010 mol min ⁻¹	Syringe delivery rate	0.875 ml min ⁻¹
$n_C - 21.2n_{Zr} - 126.8n_Y = 0$		Volume Ratio	Y:Zr 1:2.5
$n_{Hf} - 48.9n_{Zr} - 158.2n_Y = 0$		Precursor Solution	Y(OBut ⁿ) ₃ : 0.5 M
		Data	toluene 25 ml
$n_O / (n_Y + n_{Zr})$	70	Zr(OBut ⁿ) ₄ : <i>n</i> -butanol	2.23 M 62.5 ml
$n_Y / (n_Y + n_{Zr})$	0.080	Precursor Solution Molarities	0.14 M Y 1.48 M Zr
$n_{O,min} - 5.3n_{Zr} - 3n_Y = 0$	0.0051	Oxygen Flow Rate	1200 sccm

Table 7-2. Crystallite size and Composition% of Tetragonal YSZ for Coatings

T (°C)	Crystallite size	Percentage of Tetragonal YSZ
690	21.7 ± 1.0	10.5
770	47.9 ± 0.8	90.2
845	50.4 ± 1.9	35.3
925	31.1 ± 1.1	21.7
960	20.7 ± 1.3	11.0
1005	18.2 ± 1.2	4.8

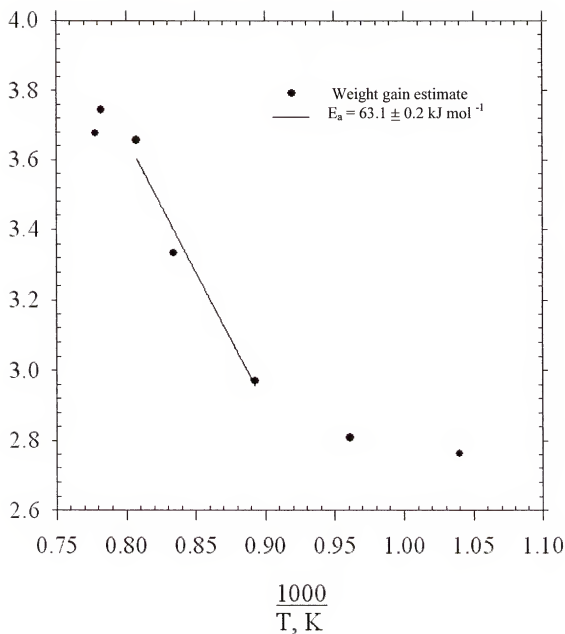


Figure 7-1. Arrhenius plot of the growth rate of the YSZ coatings based on weight gain measurement.

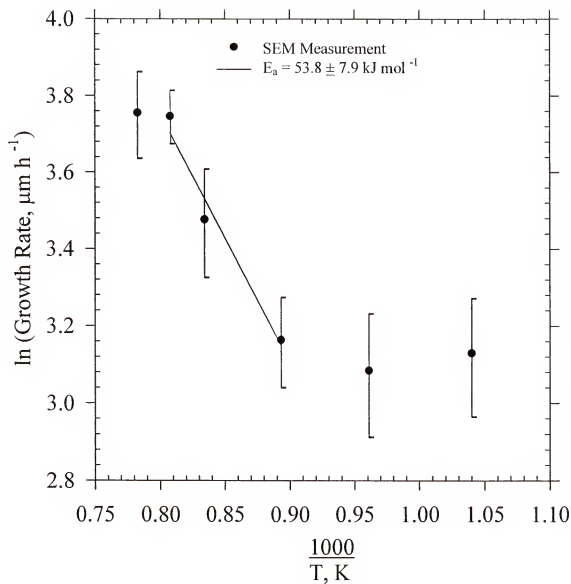


Figure 7-2. Arrhenius plot of the growth rate of the YSZ coatings based on cross-sectional SEM measurement.

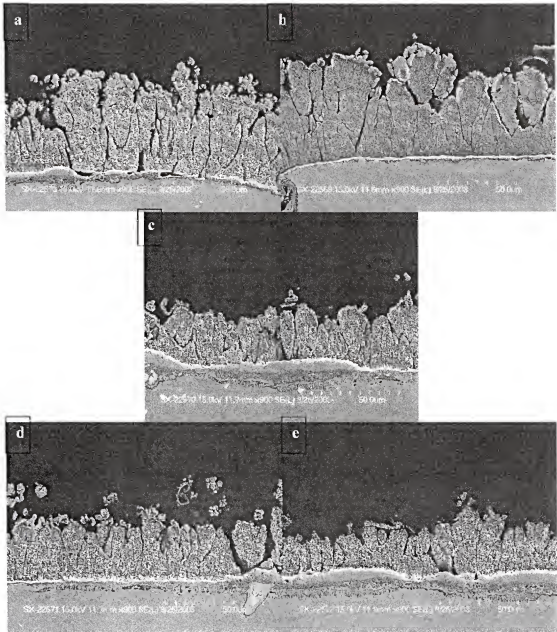


Figure 7-3. Scanning electron micrograph of YSZ coating deposited at 690°C. Micrographs taken at a) 0, b) 0.5, c) 1.0, d) 1.5, and e) 2.0 cm over the 2 cm sample diameter.

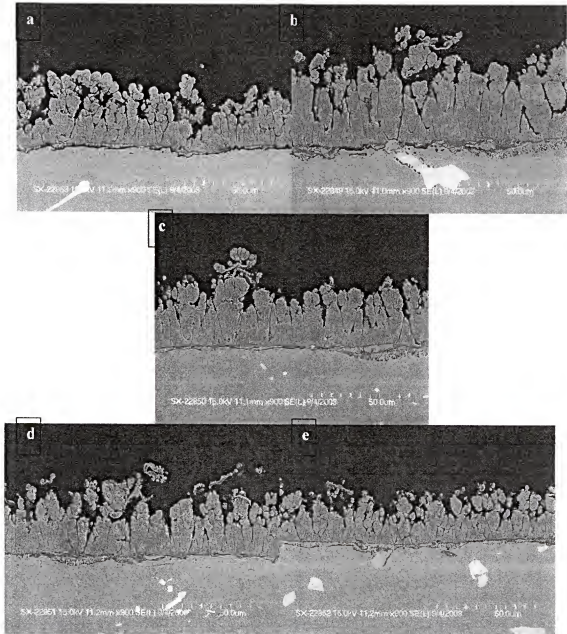


Figure 7-4. Scanning electron micrograph of YSZ coating deposited at 770°C. Micrographs taken at a) 0, b) 0.5, c) 1.0, d) 1.5, and e) 2.0 cm over the 2 cm sample diameter.

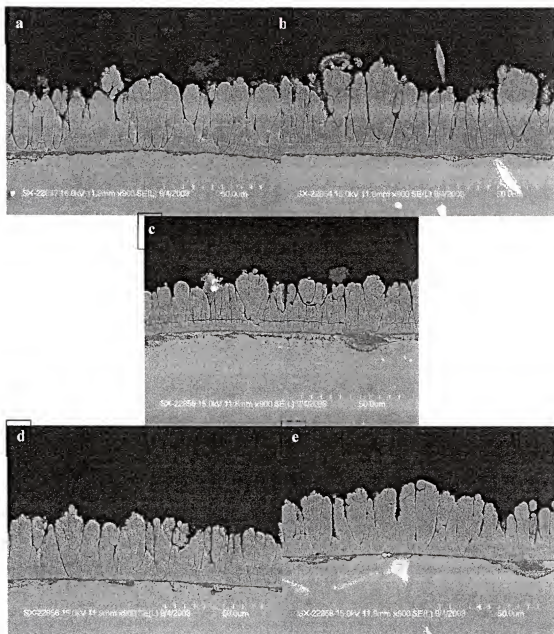


Figure 7-5. Scanning electron micrograph of YSZ coating deposited at 845°C. Micrographs taken at a) 0, b) 0.5, c) 1.0, d) 1.5, and e) 2.0 cm over the 2 cm sample diameter.

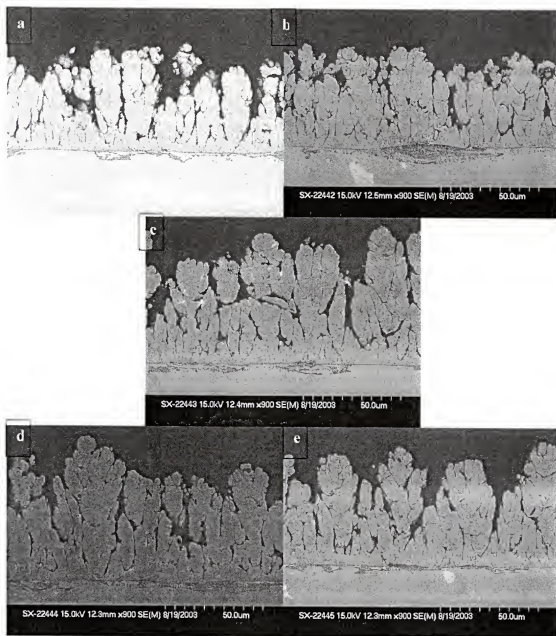


Figure 7-6. Scanning electron micrograph of YSZ coating deposited at 925°C. Micrographs taken at a) 0, b) 0.5, c) 1.0, d) 1.5, and e) 2.0 cm over the 2 cm sample diameter.

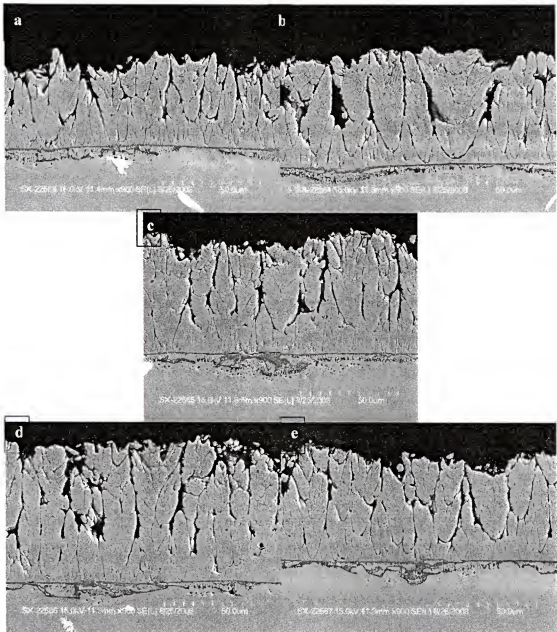


Figure 7-7. Scanning electron micrograph of YSZ coating deposited at 965°C. Micrographs taken at a) 0, b) 0.5, c) 1.0, d) 1.5, and e) 2.0 cm over the 2 cm sample diameter.

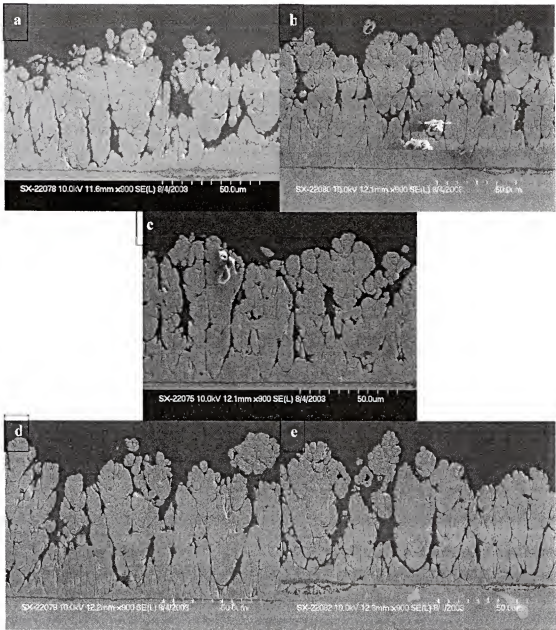


Figure 7-8. Scanning electron micrograph of YSZ coating deposited at 1005°C. Micrographs taken at a) 0, b) 0.5, c) 1.0, d) 1.5, and e) 2.0 cm over the 2 cm sample diameter.

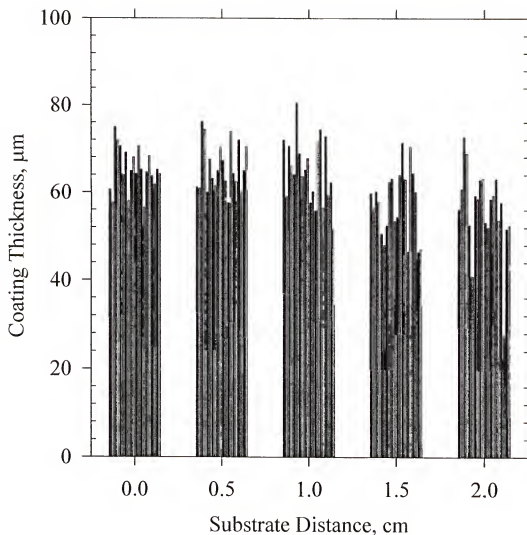


Figure 7-9. Plot of coating thickness over the coating cross-section. The substrate distance represents the point over the substrate cross-section. Distances 0.0 to 2.0 correspond to micrographs a to e, respectively, in Figure 7-8. The points labeled 0.0 and 2.0 are the substrate edge and 1.0 is the substrate center.

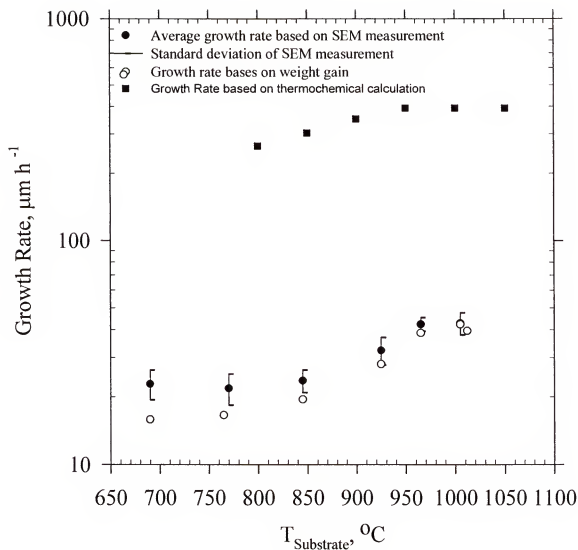


Figure 7-10. Plot of growth rate as a function of substrate temperature as determined by three methods. Conditions for both experimental and thermodynamic conditions are given in Table 7-1

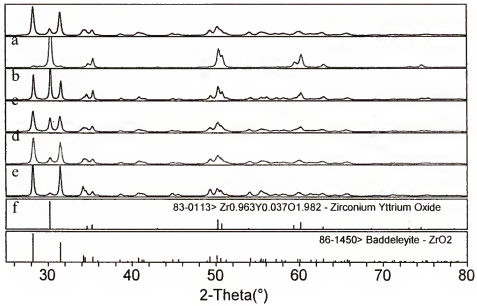


Figure 7-11. Result of x-ray diffraction of samples after calcine at 1000°C for 4 hours. Samples deposited prior to calcine at a) 690°C, b) 770°C, c) 845°C, d) 925°C, e) 965°C, f) 1005°C. Sample patterns compared against known peak reflections for tetragonal YSZ (PDF card # 83-0113) and monoclinic zirconia (baddeleyite) (PDF card # 86-1450).

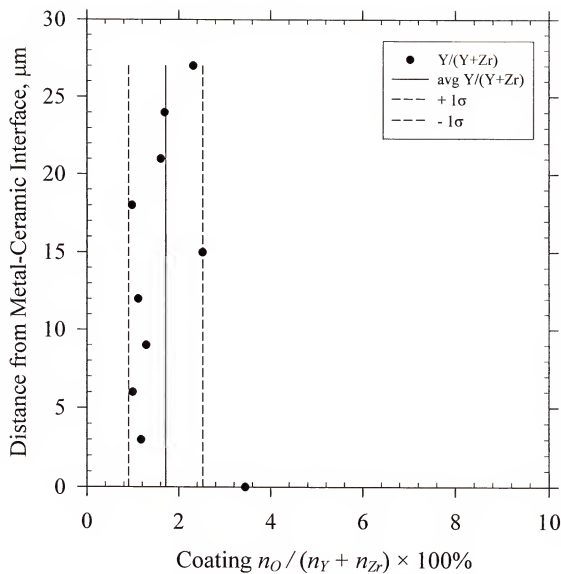


Figure 7-12. Plot showing $Y/(Y+Zr)$ coating ratio through the coating thickness at 690°C

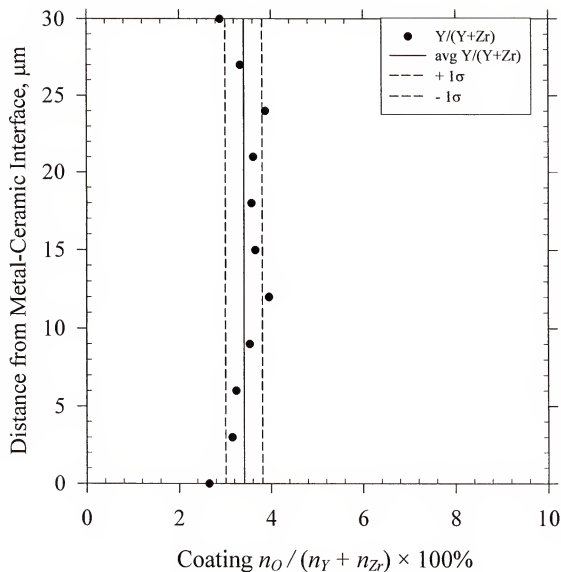


Figure 7-13. Plot showing $Y/(Y+Zr)$ coating ratio through the coating thickness at 770°C .

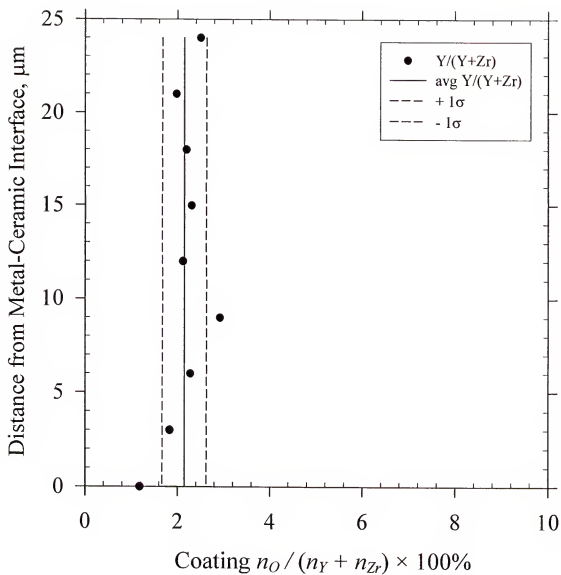


Figure 7-14. Plot showing $Y/(Y+Zr)$ coating ratio through the coating thickness at 845°C .

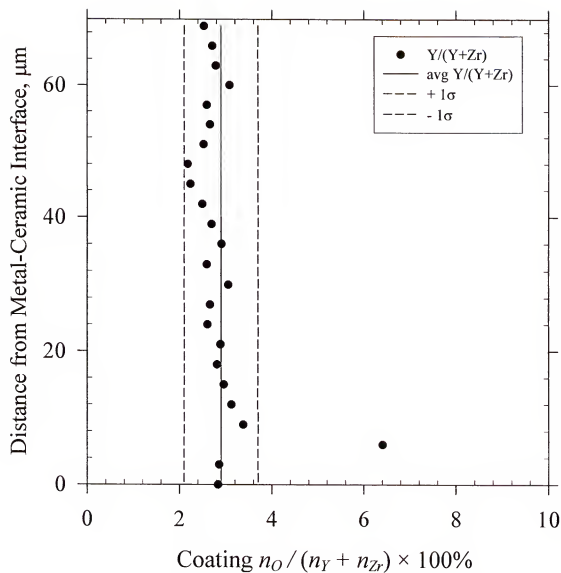


Figure 7-15. Plot showing $Y/(Y+Zr)$ coating ratio through the coating thickness at 925°C .

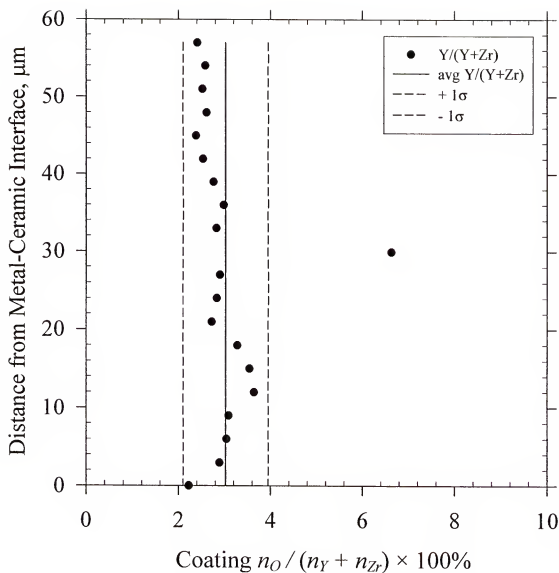


Figure 7-16. Plot showing $Y/(Y+Zr)$ coating ratio through the coating thickness at 965°C .

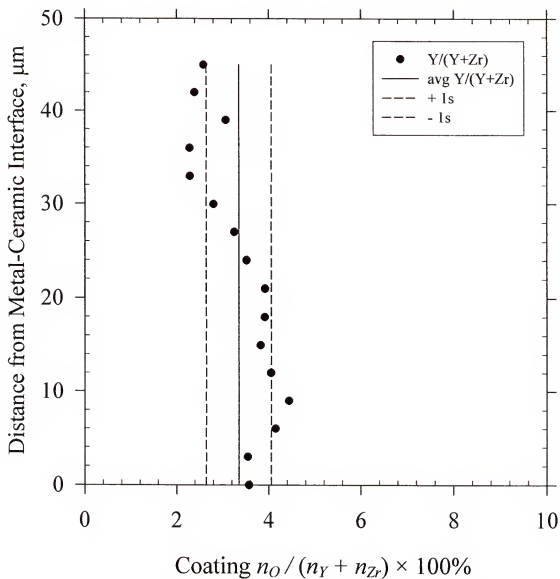


Figure 7-17. Plot showing $Y/(Y+Zr)$ coating ratio through the coating thickness at 1005°C .

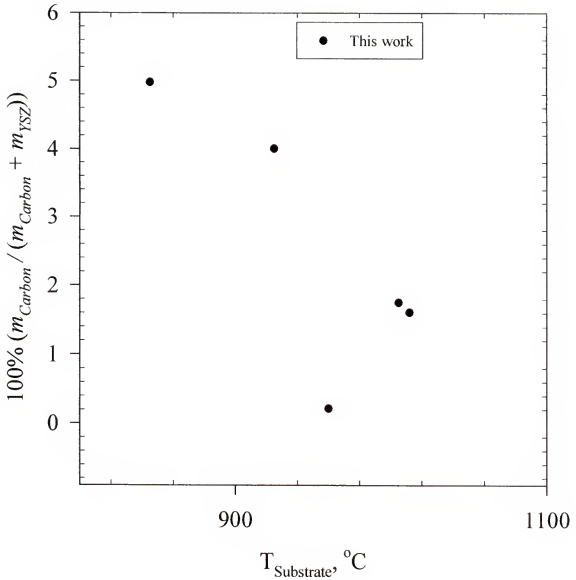


Figure 7-18. Mass of carbon (m_{Carbon}) relative to the mass of YSZ (m_{YSZ}) formed. The mass of deposited carbon was determined by noting color change and weight change of the as-deposited coatings after calcination at 1000 $^{\circ}C$ for 4 hours. All carbon was “burned-off” after calcination.

CHAPTER 8 SUMMARY, CONCLUSIONS AND FUTURE WORK

8.1 Summary and Conclusions

In this work, CVD was investigated as a commercially viable alternative to EB-PVD. The effort in this work included an equilibrium analysis, coating deposition experiments, and coating analysis. For the equilibrium analysis, the software package ThermoCalc was used to predict and optimize CVD conditions used for YSZ deposition. For coating deposition experiments, a vertical, cold-wall reactor was used to promote high growth rates. Finally, coating analysis included crystal structure analysis by XRD, morphological analysis by SEM, and compositional analysis by EPMA.

Equilibrium modeling proved to be very useful. The species and phases of interest were defined by thermochemical properties (heat of formation and enthalpy at 298.15 K and 1 bar and the specific heat constants). The thermochemical properties of the pure substances and solid solutions of the YSZ phase diagram were compiled into a database. Then, CVD conditions were optimized based on the resulting species or phases that formed.

In the case of chloride CVD, it was found that high oxygen content ($n_O / (n_Y + n_{Zr}) > 8$), low hydrogen content ($n_H / n_C < 1$), and high temperatures ($T > 950^\circ\text{C}$) ensured pure metal oxide formation of tetragonal YSZ. The need for high system oxygen was due to the stoichiometric need to satisfy the Zr atom to form zirconia and the relatively high oxygen potential required for oxidizing yttrium atoms (Minet *et al.* 1986, Sipp *et al.*

1992b). The high system oxygen was also necessary to ensure that efficient precursor utilization occurred. If sufficient oxygen was not present, secondary phase formation of YCl_3 , ZrC , C , monoclinic zirconia (αZrO_2), or monoclinic YSZ (Mss) could also form and diminish the properties of the tetragonal YSZ coatings. If sufficient system hydrogen is present, formation of solid carbon containing species (C and ZrC) were promoted. Solid carbon formed due to the high system hydrogen reducing CO_2 to CO and H_2O , and further reducing CO to H_2O and solid carbon (Minet *et al.* 1987). The formation of ZrC occurred in high system hydrogen because of the potential of hydrogen to drive the reaction of ZrCl_4 with CH_4 at high temperature ($> 1200^\circ\text{C}$) to form ZrC (Ikawa 1972). Finally, high temperature ($> 950^\circ\text{C}$) was required for tetragonal YSZ formation according to the assessed phase diagram (Du *et al.* 1992).

In the case of MOCVD, higher system oxygen (as compared to chloride CVD) was required to ensure pure oxide formation of tetragonal YSZ. The oxygen requirement was $n_{\text{O}} / (n_{\text{Y}} + n_{\text{Zr}}) > 1050$ for Y- and Zr- β -diketonates and $n_{\text{O}} / (n_{\text{Y}} + n_{\text{Zr}}) > 30$ for the Y- and Zr-*n*-butoxide precursors. The reason for the high system oxygen was due to the relatively high atomic carbon to metal ratio in the metal-organic precursors and solvents. In agreement with chloride CVD, the use of high temperature ($> 950^\circ\text{C}$) is necessary to ensure deposition of tetragonal YSZ.

The optimized conditions from the equilibrium analysis led to the successful experimental growth of zirconia in chloride CVD. The growth rate, however, was low ($5.5 \mu\text{m h}^{-1}$) with a low overall efficiency ($< 1\%$). This efficiency was defined as the ratio of the moles of Zr incorporated in the coating to the moles of Zr inlet to the reaction zone (via ZrCl_3 or ZrCl_4). The low efficiency was attributed to the use of atmospheric

pressure and evidence of significant homogeneous nucleation. Deposition at atmospheric pressure promotes significant gas phase interaction. If the gas flow becomes too hot above the substrate, significant powder formation can occur and deposition can occur on the chamber wall downstream of the substrate. Since growth was minimal, these experiments were abandoned due to the additional difficulties with incorporating yttrium.

MOCVD using β -diketonate precursors and oxygen carrier/reactant gas yielded tetragonal YSZ with higher growth rates ($\sim 14 \mu\text{m h}^{-1}$) and improved efficiencies ($\sim 10\%$). The coatings were tetragonal in crystal structure with a preferred (1 0 1) orientation. Unlike chloride precursors, however, deposition of YSZ using MOCVD had small traces of carbon ($\sim 1\text{-}2\%$). When the coatings were calcined, this carbon disappeared. The coatings appeared to have a layered microstructure with the coating thickness varying by approximately 10-15% over its cross-section.

Despite the benefits of using β -diketonate precursors, the growth rates were too low for TBC applications. Thus, highly soluble Y- and Zr-*n*-butoxide precursors were used. The improved solubility and high oxygen flow rate led to a tripling of the growth rate ($43 \mu\text{m h}^{-1}$). Further, the coating microstructure was columnar with coating growth thicknesses about 15-20% of their average thickness over the sample cross-section. Despite the high growth rates and beneficial columnar structure, the YSZ coatings had low yttrium content. The $n_Y / (n_Y + n_{Zr})$ ratio in the coating was at best 45% of the intended $n_Y / (n_Y + n_{Zr})$ ratio in the precursor solution. This was deleterious because the low yttrium content could allow the coating to phase transform during thermal cycling.

MOCVD demonstrated several advantages over chloride CVD. First, the yttrium precursors were relatively easier to utilize as compared to YCl_3 . This was owed to their

high solubility and relatively easy transport into the reaction chamber by use of the AALD method (Garcia *et al.* 1992). This means that the deposition rate is limited by precursor solution solubility and precursor solution delivery rate. The increased precursor transport was observed when a relatively high growth rate in this work was obtained at the same activation energy as compared to the literature. For example, in the MOCVD of tetragonal YSZ using b-diketonate precursors, the activation energies were very close for Garcia *et al.* (1992) ($E_a = 58 \text{ kJ mol}^{-1}$) and this work ($E_a = 59.89 \text{ kJ mol}^{-1}$). The close agreement suggested that the reaction pathway was the same and the solvent played no role in the tetragonal YSZ formation. Yet, the growth rate in this work was almost 15 times higher in this work as compared to Garcia *et al.* (1992). Thus, precursor transport to the substrate was improved, resulting in higher growth rates using the AALD method.

MOCVD did have one disadvantage as compared to chloride CVD. This had to do with carbon formation. The cause of carbon formation was not studied in this work, however, Cameron and George (2000) and Igumenov (2001) mention that high oxygen content and high temperature did minimize the formation of carbon. This was evident in Chapter 7 where the carbon content was seen to decrease with increasing temperature in this work. It is reasonable to suggest that the use of an oxygen carrier/reagent gas minimizes carbon formation by promoting the formation of volatile CO and CO₂ species at high temperature. However, without mass spectrometry studies, a reason for carbon deposition cannot be given.

Finally, use of the stagnation-plane flow injector did not promote high growth rate coatings. Although it promoted better coating uniformity, the stagnation-plane flow

injector was not useful since significant clogging of the injector occurred with highly soluble precursors.

Overall, MOCVD using the Y- and Zr-*n*-butoxide precursors is a viable method for producing high growth rate coatings with adequate coating uniformity. The high growth rates ($43 \mu\text{m h}^{-1}$) achieved in this work proves that a cost-effective alternative to EB-PVD can be used for thermal barrier applications.

8.2 Recommendations for Future Work

8.2.1 Improvements in Coating Deposition

Improvements in coating deposition are needed to ensure deposition of single phase, tetragonal YSZ. Currently, the Y precursor content is insufficient for deposition of single phase tetragonal YSZ. Since less than half of the yttrium content in the gas phase was incorporated in the coating. This means that doubling the yttrium precursor concentration in the liquid precursor solution may help to double the yttrium content in the coating. This can be accomplished in a growth regime limited by mass-transfer since the yttrium incorporation in the coating is linear with yttrium gas phase presence in this growth regime. A coating was deposited at 1005°C in which the yttrium content was doubled ($n_Y / (n_Y + n_{Zr}) = 16$) in the liquid precursor solution. Initial XRD results (Figure 8-1) show the good agreement between the sample pattern and the PDF card (# 78-1808), which contains phase information for tetragonal YSZ.

Another improvement that can also be made is too increasing the pre-oxidation time for the bond coat. This will allow the alumina scale thickness to increase (Brady *et al.* 2000) such that YSZ formation can occur on alumina. The deposition of YSZ on

alumina has been observed in this work (Chapter 6) to improve coating adherence to the substrate.

8.2.2 Thermal Cycle Testing of Coatings

Although high growth rates are achievable in MOCVD YSZ coatings, the proof of the benefit of using MOCVD will be the demonstration of its resistance to delamination owed to thermal cycling.

Normally, the coating is subjected to at least one thermal cycle when they are calcined in air at 1000°C for 4 hours after deposition. The coatings remain adherent after calcine, which is beneficial. This means that additional thermal cycling must be performed to determine the longevity of the coating attachment.

The coatings are thermally cycled to test the lifetime of the YSZ attachment to the blade material. The thermal cycling unit is shown in Figure 8-2. An overview of how the testing unit operates was discussed in Chapter 2 and can be found in the work of several authors (Pint *et al.* 1998, Zhang *et al.* 2001, Haynes *et al.* 2001). If the coatings do not suffer catastrophic weight loss after several hundred 1-hr thermal cycles, the coatings may be suitable for application in actual blade testing in a gas turbine.

Upon initial testing of these coatings, the lifetime was not very high. A calcined coating of YSZ (with higher yttrium content) was tested in the thermal cycling unit (Figure 8-2). The sample was hung onto a mantle (Figure 8-3) and was then drawn vertically into the testing unit. The coatings underwent 1-hr thermal cycles, where they were drawn into the testing unit at 1200°C (hot-insertion method). The coatings remained at temperature for 50 minutes, and then were drawn out of the unit for 10 minutes at 25°C, thus completing a 1-hr cycle. This process was repeated for 20 cycles

and then the samples were weighed for weight gain or loss. The samples were discontinued from thermal cycling when they suffered significant weight loss.

Initial testing of the YSZ coated bond coat was compared to an uncoated bond coat (Figure 8-4). On one hand, the uncoated alloy bond coat endured for approximately 300 1-hr thermal cycles. The uncoated sample underwent a gradual weight gain (owed to the slow growth of the alumina-scale) with increasing 1-hr thermal cycles. On the other hand, the alloy substrate coated with YSZ had a steady decrease in the weight loss and only endured for 100 1-hr thermal cycles. The coating exhibited separation and delamination within the YSZ-alumina scale interface (Figure 8-5). This indicated that insufficient pre-oxidation time (~ 10 minutes) caused the attachment of YSZ to the bond coat to be inadequate. Thus, the initial coatings testing showed that the adherence of YSZ to the alumina scale was inadequate.

8.2.3 Determination of a Growth Mechanism

The determination of a growth mechanism for YSZ growth using the Y- and Zr-*n*-butoxide precursors has not been studied. Mechanistic data are lacking with these precursors only due to their recent introduction by Aldrich Chemicals, Inc. There are five immediately foreseeable benefits to studying the growth of YSZ using these precursors: (1) determining the decomposition of both Y and Zr precursors, (2) determining why yttrium content in the coating was less than half of the intended yttrium amount in the liquid precursor solution, (3) determining the role of the toluene and *n*-butanol solvents during CVD, (4) determine the role that additional oxygen plays, and (5) determine the root causes for carbon deposition while using these precursors.

The approach undertaken is three-fold. First, precursor studies need to be performed to obtain reliable data on the decomposition temperatures. This can involve the use of differential thermal analysis (DTA) to study the temperatures at which decomposition of the Y- and Zr-*n*-butoxide precursors occurs (Matsuzaki *et al.* 1999). This technique involves the detection of released heat owed to the exothermic decomposition of the precursor in flowing air at a steadily increasing temperature ($1^{\circ}\text{C min}^{-1}$).

A definite need to run separate CVD experiments for each precursor with and without the solvent and with and without the addition of oxygen would be quite beneficial. First, studying the deposition of yttria or zirconia using the Y- or Zr-*n*-butoxide precursors, respectively, in a high flux environment without addition of oxygen or solvent would isolate the activation barrier and temperature range for surface-reaction limited growth. Then, CVD studies can be performed on the use of a solvent to assist in precursor transport. Finally, the addition of oxygen can be used to study the effect of oxygen on the resulting deposit. Finally, if water vapor can be metered into the reaction chamber in a precise fashion, the effect of this water vapor on carbon formation and surface-reactions can be studied.

Finally, mass spectrometry can be used to study the reaction mechanism. (Lopeava *et al.* 2002) Mass spectrometry is a method of analyzing a gas mixture by studying the mass-to-charge ratio to identify the various gas species that may be present in that gas mixture. Mass spectrometry is a powerful tool in identifying species in the gas phase that are a product of the surface reactions and by-product desorption or gas phase

reactions involved in CVD. This can be a valuable tool in determining reaction pathways for the deposition of tetragonal YSZ. (Lopeava *et al.* 2002)

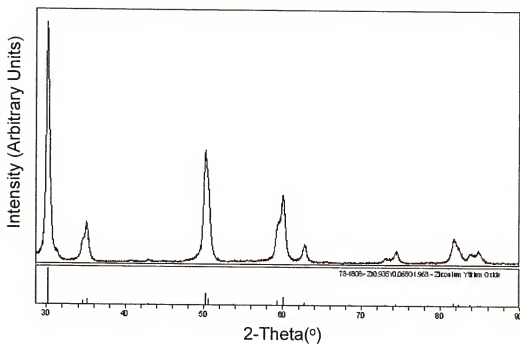


Figure 8-1. XRD result of coating with adjusted yttrium content. The sample pattern is given with the tetragonal YSZ PDF card (# 78-1808) given below the sample pattern.

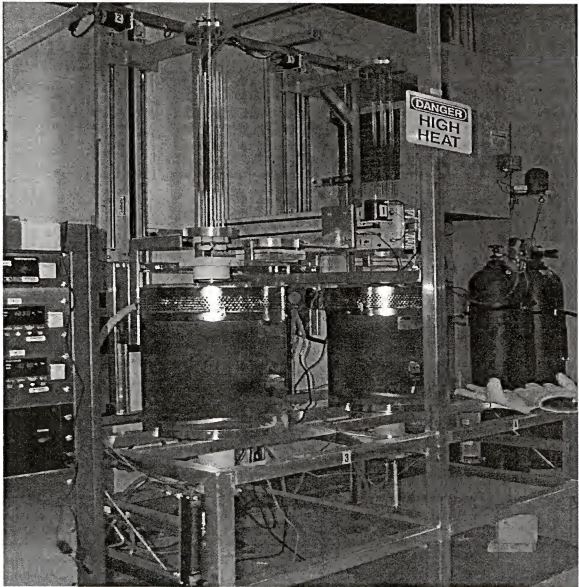


Figure 8-2. Oxidation testing unit (black cylinders) for thermal cycling studies of TBC materials. *Courtesy of B. A. Pint, Oak Ridge National Laboratory, Oak Ridge, TN, 37830.*

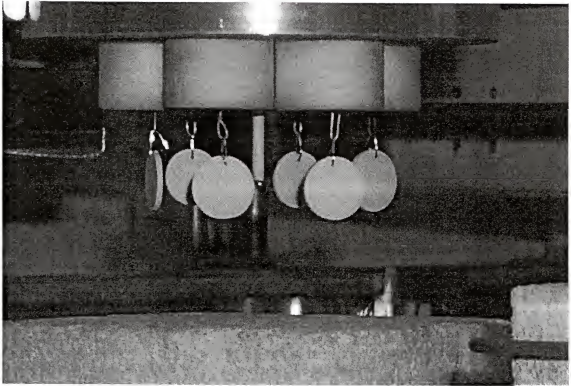


Figure 8-3. Sample mounting for thermal cyclic testing at Oak Ridge National Laboratory. This mantle was drawn in with the specimens hanging into the testing unit shown in Figure 8-2. *Courtesy of B. A. Pint, Oak Ridge National Laboratory, Oak Ridge, TN, 37830.*

Mass Change vs. Cycle

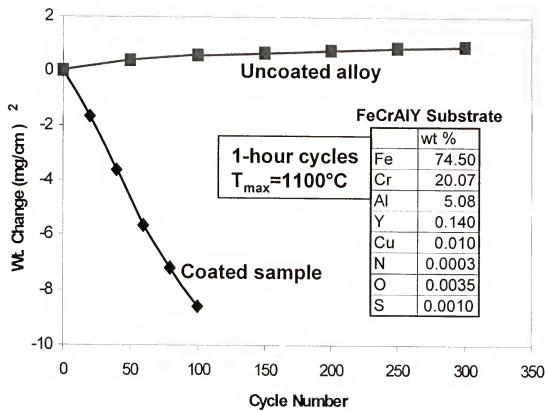


Figure 8-4. Plot showing the lifetime of uncoated and YSZ coated alloy bond coats.

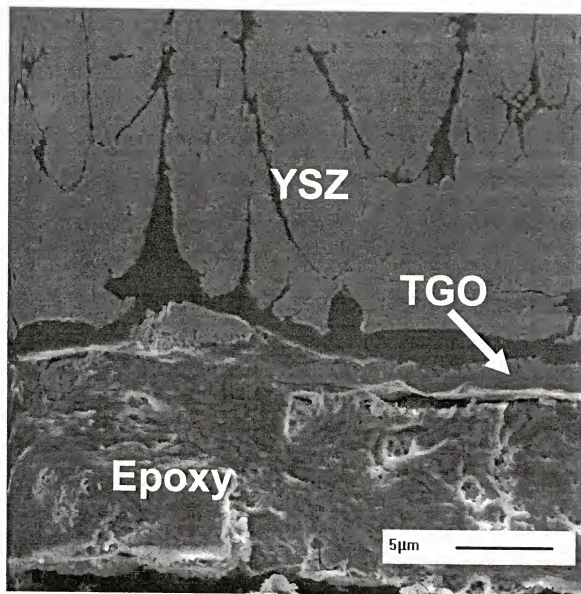


Figure 8-5. Electron micrograph of delaminated YSZ coating.

APPENDIX A PDF CARDS FOR USE IN X-RAY DIFFRACTION ANALYSIS

Details are given in Table A-1 to Table A-4 with regard to PDF cards used for XRD analysis (ICCD 2002). The cards given in these tables refer to tetragonal YSZ at two differing mole percentages of $\text{YO}_{1.5}$, baddelyite (monoclinic zirconia), and corundum ($\alpha\text{-Al}_2\text{O}_3$) substrates. Please refer to the *JADE* software package and the *ICCD* for further information on these PDF cards (ICCD 2002).

Table A.1. PDF card information for PDF#48-0224

2-Theta	d(Å)	I(f)	h	k	l	Theta	1/(2d)	2pi/d n ²
30.17	2.9597	100	1	0	1	15.085	0.1689	2.1229
34.692	2.5836	7	0	0	2	17.346	0.1935	2.4319
35.115	2.5534	12	1	1	0	17.558	0.1958	2.4607
43.011	2.1012	<1	1	0	2	21.506	0.238	2.9903
50.191	1.8162	35	1	1	2	25.095	0.2753	3.4596
50.503	1.8057	22	2	0	0	25.251	0.2769	3.4797
53.125	1.7226	<1	0	0	3	26.562	0.2903	3.6476
53.722	1.7048	<1	2	0	1	26.861	0.2933	3.6856
59.405	1.5546	10	1	0	3	29.703	0.3216	4.0418
59.967	1.5413	18	2	1	1	29.984	0.3244	4.0765
62.727	1.48	5	2	0	2	31.364	0.3378	4.2455
73.202	1.2919	1	0	0	4	36.601	0.387	4.8635
74.23	1.2765	3	2	2	0	37.115	0.3917	4.9221
81.662	1.1781	6	2	1	3	40.831	0.4244	5.3333
82.151	1.1723	4	3	0	1	41.076	0.4265	5.3596
83.859	1.1527	2	1	1	4	41.93	0.4337	5.4507
84.597	1.1446	2	2	2	2	42.298	0.4368	5.4896
84.834	1.142	2	3	1	0	42.417	0.4378	5.5021

PDF#48-0224: QM=Star(S); d=Diffraction; I=Diffraction

Yttrium Zirconium Oxide

Zr0.92 Y0.08 O1.96 White

Radiation=CuKα1 Lambda=1.54056 Filter=Graph

Calibration=External(Si) 2θ=30.170-84.834 I/Ic(RIR)=4.71

Ref: Zubkov, V., Inst. of Solid State Chemistry, Ural Branch of Russian Academy of Sciences, Ekaterinburg, Russia.

ICDD Grant-in-Aid (1997)

Tetragonal - (Unknown), P42/nmc (137) Z=2 mp=

CELL: 3.611 x 3.611 x 5.1675 <90.0 x 90.0 x 90.0> P.S=tP5.92 (?)

Density(c)=6.031 Density(m)=5.900 Mwt=122.39 Vol=67.38

F(17)=261.5(0.033,20/1)

Ref: Ibid.

Strong Lines: 2.96/X 1.82/4 1.81/2 1.54/2 2.55/1 1.55/1 2.58/1 1.18/1 1.48/1 1.17/1

NOTE: Chemical analysis (wt.%): Zr 68.6, Y 5.8, O 25.6.

*Not permitted by space group.

Table A-2. PDF card information for PDF#74-1081

2-Theta	d(Å)	I(f)	h k l			Theta	1/(2d)	2pi/d n^2
25.583	3.4791	58	1	1	0	12.792	0.1437	1.806
35.156	2.5506	100	1	2	1	17.578	0.196	2.4634
37.791	2.3786	43.3	1	1	0	18.895	0.2102	2.6416
41.679	2.1652	1.1	2	2	2	20.839	0.2309	2.9018
43.367	2.0848	86.7	1	2	0	21.683	0.2398	3.0138
46.195	1.9635	0.5	0	2	0	23.097	0.2546	3.1999
52.567	1.7395	45.6	2	2	0	26.283	0.2874	3.612
57.511	1.6012	68.1	1	2	3	28.756	0.3123	3.9241
59.764	1.5461	2.5	1	2	0	29.882	0.3234	4.064
61.154	1.5142	1.4	1	2	1	30.577	0.3302	4.1494
61.308	1.5108	9.8	3	3	2	30.654	0.331	4.1589
66.541	1.4041	31.4	1	3	0	33.271	0.3561	4.4749
68.238	1.3733	42.3	2	1	1	34.119	0.3641	4.5754
70.439	1.3356	1.1	2	3	0	35.219	0.3743	4.7042
74.314	1.2753	1.9	2	4	2	37.157	0.3921	4.9269
76.88	1.239	10.8	3	4	3	38.44	0.4036	5.0712
77.248	1.234	6.5	3	4	2	38.624	0.4052	5.0916
80.44	1.1929	0.7	1	2	4	40.22	0.4192	5.2672
80.735	1.1893	4.4	2	2	0	40.367	0.4204	5.2832
83.244	1.1597	0.2	3	3	0	41.622	0.4311	5.418
84.392	1.1468	1.6	1	3	1	42.196	0.436	5.4788
85.178	1.1382	0.1	2	2	1	42.589	0.4393	5.5201
86.39	1.1253	2.5	1	3	0	43.195	0.4443	5.5834
86.526	1.1239	3.3	3	4	1	43.263	0.4449	5.5904
89.013	1.0989	4	4	4	2	44.506	0.455	5.718

PDF#74-1081: QM=Calculated(C); d=Calculated; I=Calculated

Corundum

Al₂O₃Radiation=CuKα₁ Lambda=1.54060 Filter=

Calibration= 2θ=25.583-89.013 I/Ic(RIR)=0.99

Ref: Calculated from ICSD using POWD-12++ (1997)

Rhombohedral - (Unknown), R-3c (167) Z=2 mp=

CELL: 5.128 x 5.128 x 5.128 <55.27 x 55.27 x 55.27> P.S=hR10 (Al₂O₃)

Density(c)=3.989 Density(m)=3.39A Mwt=101.96 Vol=254.61

F(25)=999.9(0002,35/0)

Ref: Saalfeld, H.

Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem., v120 p342 (1964)

Strong Lines: 2.55/X 2.08/9 1.60/7 3.48/6 1.74/5 2.38/4 1.37/4 1.40/3 1.24/1 1.51/1

FIZ=026790: At least one TF missing.

See PDF 43-1484.

Table A-3. PDF card information for PDF#83-0113

2-Theta	d(Å)	I(f)	h	k	l	Theta	1/(2d)	2pi/d n ²
30.204	2.9565	100	1	0	1	15.102	0.1691	2.1252
34.608	2.5896	8.1	0	0	2	17.304	0.1931	2.4263
35.219	2.5461	13.1	1	1	0	17.609	0.1964	2.4677
42.985	2.1024	1	1	0	2	21.493	0.2378	2.9886
50.208	1.8156	32.8	1	1	2	25.104	0.2754	3.4607
50.661	1.8004	17.3	2	0	0	25.33	0.2777	3.4899
53.866	1.7006	0.1	2	0	1	26.933	0.294	3.6947
59.313	1.5568	11.3	1	0	3	29.657	0.3212	4.0361
60.122	1.5377	21.5	2	1	1	30.061	0.3252	4.086
62.809	1.4783	5.4	2	0	2	31.404	0.3382	4.2504
68.565	1.3675	0.3	2	1	2	34.283	0.3656	4.5947
73.01	1.2948	1.7	0	0	4	36.505	0.3862	4.8526
74.465	1.2731	4	2	2	0	37.233	0.3927	4.9354
78.423	1.2184	0.2	1	0	4	39.212	0.4104	5.1567
81.706	1.1776	7.5	2	1	3	40.853	0.4246	5.3357
82.411	1.1693	3.7	3	0	1	41.206	0.4276	5.3736
83.733	1.1542	2.7	1	1	4	41.866	0.4332	5.4439
84.786	1.1425	2.2	2	2	2	42.393	0.4376	5.4996
85.137	1.1387	2.2	3	1	0	42.569	0.4391	5.518

PDF#83-0113: QM=Calculated(C); d=Calculated; I=Calculated

Zirconium Yttrium Oxide

Zr0.963 Y0.037 O1.982

Radiation=CuKα1 Lambda=1.54060 Filter=

Calibration= 2θ=30.204-85.137 I/Ic(RIR)=10.17

Ref: Calculated from ICSD using POWD-12++ (1997)

Tetragonal - Powder Diffraction, P42/nmc (137) Z=2 mp=

CELL: 3.6008 x 3.6008 x 5.1793 <90.0 x 90.0 x 90.0> P.S=tP5.96 (?)

Density(c)=6.074 Density(m)=5.98A Mwt=122.85 Vol=67.15

F(19)=999.9(.0001,20/0)

Ref: Argyriou, D.N., Howard, C.J.

J. Appl. Crystallogr., v28 p206 (1995)

Strong Lines: 2.96/X 1.82/3 1.54/2 1.80/2 2.55/1 1.56/1 2.59/1 1.18/1 1.48/1 1.27/1

FIZ=079197: RVP.

F There is a 21 mass% admixture of cubic phase.

ITF See PDF 80-2187.

Table A-4. PDF card information for PDF#86-1450

2-Theta	d(Å)	I(f)	h k l			Theta	1/(2d)	2pi/d n ²
17.444	5.0795	7	1	0	0	8.722	0.0984	1.237
24.054	3.6967	17.3	0	1	1	12.027	0.1353	1.6997
24.451	3.6376	13	1	1	0	12.225	0.1375	1.7273
28.182	3.1638	100	-1	1	1	14.091	0.158	1.9859
31.472	2.8402	67.8	1	1	1	15.736	0.176	2.2122
34.166	2.6222	20.9	0	0	2	17.083	0.1907	2.3962
34.387	2.6058	13.3	0	2	0	17.194	0.1919	2.4112
35.31	2.5398	15.1	2	0	0	17.655	0.1969	2.4739
35.906	2.499	3	-1	0	2	17.953	0.2001	2.5143
38.547	2.3336	5.5	0	2	1	19.274	0.2143	2.6925
39.435	2.2831	1	2	1	0	19.718	0.219	2.7521
39.978	2.2533	0.3	-1	1	2	19.989	0.2219	2.7884
40.733	2.2133	13	-2	1	1	20.367	0.2259	2.8389
41.16	2.1913	4.7	1	0	2	20.58	0.2282	2.8673
41.377	2.1803	5.1	-1	2	1	20.688	0.2293	2.8817
43.795	2.0654	0.1	1	2	1	21.897	0.2421	3.0421
44.832	2.02	7.1	1	1	2	22.416	0.2475	3.1105
45.528	1.9907	6.8	2	1	1	22.764	0.2512	3.1562
45.528	1.9907	6.8	-2	0	2	22.764	0.2512	3.1562
48.938	1.8597	1.7	-2	1	2	24.469	0.2689	3.3787
49.258	1.8484	16.6	0	2	2	24.629	0.2705	3.3993
50.113	1.8188	20.4	2	2	0	25.057	0.2749	3.4546
50.563	1.8036	11.8	-1	2	2	25.282	0.2772	3.4836
51.194	1.7829	5.4	-2	2	1	25.597	0.2804	3.5242
54.102	1.6937	11	2	0	2	27.051	0.2952	3.7097
54.102	1.6937	11	3	0	0	27.051	0.2952	3.7097
54.682	1.6771	0.7	1	2	2	27.341	0.2981	3.7464
55.28	1.6604	4.6	2	2	1	27.64	0.3011	3.7841
55.389	1.6574	9.7	0	1	3	27.695	0.3017	3.791
55.608	1.6514	7.1	-1	1	3	27.804	0.3028	3.8049
55.889	1.6437	7.7	1	3	0	27.945	0.3042	3.8225
57.175	1.6098	7.9	3	1	0	28.588	0.3106	3.9032
57.175	1.6098	7.9	-3	1	1	28.588	0.3106	3.9032
57.864	1.5922	4.7	-1	3	1	28.932	0.314	3.9461
58.278	1.5819	3.1	-2	2	2	29.139	0.3161	3.9719
59.776	1.5458	8.2	1	3	1	29.888	0.3235	4.0647
60.055	1.5393	7.1	-3	0	2	30.028	0.3248	4.0819
61.368	1.5094	5.3	1	1	3	30.684	0.3312	4.1626
61.985	1.4959	6.1	-2	1	3	30.993	0.3342	4.2003
62.845	1.4775	9.2	-3	1	2	31.422	0.3384	4.2526
62.845	1.4775	9.2	3	1	1	31.422	0.3384	4.2526
64.092	1.4517	1.3	0	2	3	32.046	0.3444	4.3281
64.293	1.4477	2.6	0	3	2	32.146	0.3454	4.3402

Table A-4. Continued

2-Theta	d(Å)	I(f)	h k l			Theta	1/(2d)	2pi/d n^2
64.293	1.4477	2.6	-1	2	3	32.146	0.3454	4.3402
64.987	1.4339	0.8	2	3	0	32.493	0.3487	4.382
65.369	1.4264	2.4	-1	3	2	32.685	0.3505	4.4049
65.696	1.4201	6.2	3	2	0	32.848	0.3521	4.4245
65.696	1.4201	6.2	2	2	2	32.848	0.3521	4.4245
65.906	1.4161	4	-2	3	1	32.953	0.3531	4.437
68.92	1.3613	2	1	3	2	34.46	0.3673	4.6155
69.444	1.3523	0.1	2	3	1	34.722	0.3697	4.6462
69.628	1.3492	0.8	1	2	3	34.814	0.3706	4.657
70.206	1.3395	0.6	-2	2	3	35.103	0.3733	4.6907
71.071	1.3253	1.9	-3	2	2	35.536	0.3773	4.7409
71.071	1.3253	1.9	3	2	1	35.536	0.3773	4.7409
71.289	1.3218	4.3	-1	0	4	35.645	0.3783	4.7535
71.961	1.3111	0.8	0	0	4	35.98	0.3814	4.7923
72.1	1.3089	1.4	-2	3	2	36.05	0.382	4.8004
72.485	1.3029	1	0	4	0	36.243	0.3838	4.8225
72.641	1.3005	1.1	2	1	3	36.32	0.3845	4.8314
73.586	1.2861	0.4	-3	1	3	36.793	0.3888	4.8855
74.685	1.2699	1.6	4	0	0	37.342	0.3937	4.9479
75.059	1.2645	4	0	4	1	37.53	0.3954	4.969
75.228	1.2621	2.2	1	4	0	37.614	0.3962	4.9786
76.443	1.245	2.1	-4	1	1	38.222	0.4016	5.0468
76.932	1.2383	0.3	-1	4	1	38.466	0.4038	5.0741
77.265	1.2338	0.7	4	1	0	38.633	0.4053	5.0926
77.38	1.2322	0.7	0	3	3	38.69	0.4058	5.099
77.566	1.2298	0.7	-1	3	3	38.783	0.4066	5.1093
78.079	1.2229	0.9	-4	0	2	39.039	0.4088	5.1377
78.079	1.2229	0.9	1	0	4	39.039	0.4088	5.1377
78.683	1.2151	0.7	-2	1	4	39.341	0.4115	5.171
78.88	1.2125	2.2	-3	3	1	39.44	0.4124	5.1819
78.88	1.2125	2.2	3	3	0	39.44	0.4124	5.1819
80.37	1.1938	0.4	2	2	3	40.185	0.4188	5.2634
80.673	1.19	0.3	-4	1	2	40.336	0.4202	5.2798
80.673	1.19	0.3	1	1	4	40.336	0.4202	5.2798
81.286	1.1826	0.5	-3	2	3	40.643	0.4228	5.313
81.603	1.1788	1.7	-1	2	4	40.801	0.4242	5.3301
82.246	1.1712	0.6	0	2	4	41.123	0.4269	5.3647
82.551	1.1677	1.8	1	3	3	41.275	0.4282	5.381
83.097	1.1614	2.3	-2	3	3	41.549	0.4305	5.4102
83.097	1.1614	2.3	4	1	1	41.549	0.4305	5.4102
83.282	1.1593	1.4	2	4	0	41.641	0.4313	5.42
83.63	1.1553	0.4	-1	4	2	41.815	0.4328	5.4385
83.864	1.1527	1.6	3	3	1	41.932	0.4338	5.4509

Table A-4. Continued

2-Theta	d(Å)	I(f)	h	k	l	Theta	1/(2d)	2pi/d n^2
83.864	1.1527	1.6	-3	3	2	41.932	0.4338	5.4509
84.123	1.1498	2	-2	4	1	42.061	0.4349	5.4646
84.123	1.1498	2	-4	2	1	42.061	0.4349	5.4646
84.873	1.1415	1.4	4	2	0	42.436	0.438	5.5041
86.153	1.1278	1.4	-3	0	4	43.077	0.4433	5.571
86.914	1.1199	0.3	1	4	2	43.457	0.4465	5.6105
87.404	1.1149	1.9	2	4	1	43.702	0.4485	5.6358
88.177	1.1071	2	-4	2	2	44.089	0.4516	5.6754
88.177	1.1071	2	1	2	4	44.089	0.4516	5.6754
88.535	1.1035	2.7	3	1	3	44.267	0.4531	5.6937
89.342	1.0956	1	2	0	4	44.671	0.4564	5.7347
89.802	1.0912	2.5	-4	1	3	44.901	0.4582	5.7579

PDF#86-1450: QM=Calculated(C); d=Calculated; I=Calculated

Baddeleyite

Zr O2

Radiation=CuKα1 Lambda=1.54060 Filter=

Calibration= 2T=17.444-89.802 I/Ic(RIR)=4.69

Ref: Calculated from ICSD using POWD-12++ (1997)

Monoclinic - Powder Diffraction, P21/c (14) Z=4 mp=

CELL: 5.14604 x 5.21162 x 5.31308 <90.0 x 99.222 x 90.0> P.S=mP12 (Co Sb2)

Density(c)=5.818 Density(m)=6.02A Mwt=123.22 Vol=140.65

F(30)=540.8(0015,37/0)

Ref: Gualtieri, A., Norby, P., Hanson, J., Hriljac, J.

J. Appl. Crystallogr., v29 p707 (1996)

Strong Lines: 3.16/X 2.84/7 2.62/2 1.82/2 3.70/2 1.85/2 2.54/2 2.61/1 3.64/1 2.21/1

FIZ=082544: RVP.

ITF Specimen from Commission on Powder Diffraction of IUCR.

APPENDIX B

CALIBRATION PROCESS FOR OPTICAL PYROMETERS

The optical pyrometers used in this work were the Ircon UX-10P and the Ircon UX-50P. The UX-10P has a working range of 900 – 3000°C, however, the instrument was calibrated for a range of 900 – 2000 Deg C. ORNL Metrology Lab currently has only one standard, a Tungsten Strip Lamp, capable of operating in this temperature range.

Figure B-1 shows the block diagram of the test setup used during the calibration. The tungsten lamp is a NIST traceable device that is characterized with a filament current versus filament temperature curve. The filament is a 4 mm wide strip. The lamp glass and filament are marked in such a manner as to provide the same view that was used during the lamp's calibration. When the marks are in alignment (as viewed through the Unit Under Test (UUT)) the same spot on the filament is viewed every time. The UUT minimum focal length of 50 cm was maintained during the test. The manufacturer's formula for spot diameter ($\text{Distance}/250$) results in a 2 mm spot at 50 cm. The lamp current is supplied by a programmable power supply capable of the 33 Amps DC required to produce the 2000°C filament temperature. The lamp current is measured using an L & N shunt and a HP Voltmeter. The measured shunt voltage is sent to custom software via an IEEE 488 bus. This voltage is converted to lamp current and compared to the desired current that was entered by the operator. Deviation from the set point results in adjustment of the power supply current via the bus so that the desired temperature is

maintained. Readings were recorded at several points in the 900 – 2000°C range with the UUT emissivity set at 0.85 and 1.0.

The UX-50P has a working range of 300 – 1000°C. The strip lamp was not suitable for this calibration due to the minimum UUT spot diameter of 20 mm. The ORNL Metrology Lab has assembled equipment that provides a black body target for this test (Figure B-2).

A spherical aluminum cavity was suspended in a fluidized sand bath to provide isothermal conditions in the cavity. The bath temperature is monitored using a NIST traceable Type S thermocouple and a custom thermocouple measurement system. Once the bath is stabilized, readings are taken with the UUT having an emissivity setting of 1.0. Two points were measured and reported, 287 and 568 Deg C. Detailed information concerning the performance of the UUTs and the traceable standards used can be found on the Calibration Reports provided to the customer.

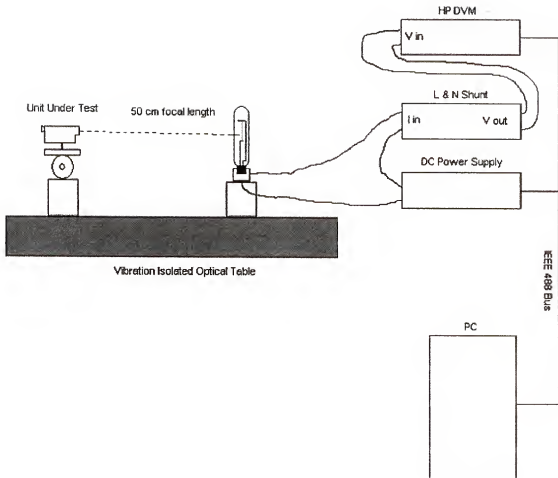


Figure B-1. Calibration test setup.

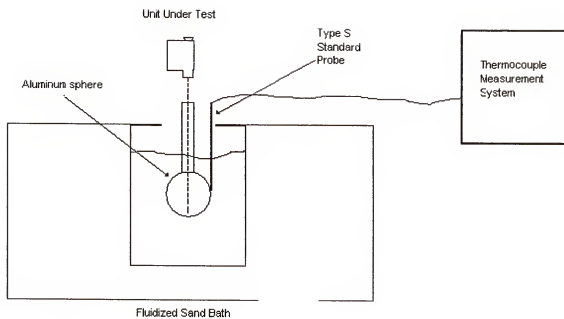


Figure B-2. Experimental setup for black-body test.

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Venu Varanasi studied for his doctoral thesis in the chemical engineering department at the University of Florida. His career goals include becoming a researcher who has fundamental and advanced understanding of the field of chemical engineering. Upon entering the University of Florida, he was awarded the University's Hawkins Fellowship and was appointed to the Dissertation Research Level Program of the Higher Education Research Experiences (HERE) at the Oak Ridge National Laboratory (ORNL). Recently, he was awarded the National Institutes of Health Post-Doctoral Fellowship for research work on dental and cranio-facial implants at the University of California in San Francisco.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


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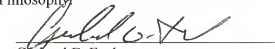
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